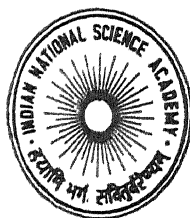
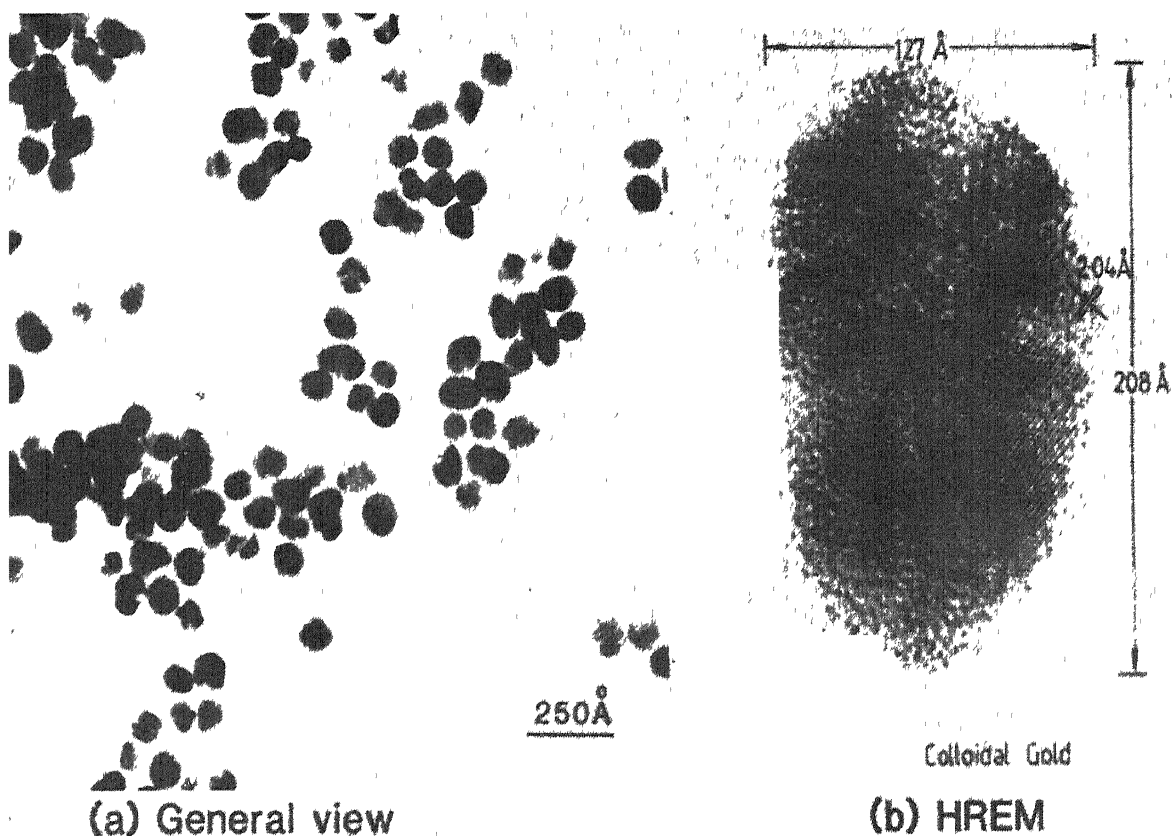


ADVANCES IN SOLID STATE CHEMISTRY

Edited by
C N R Rao



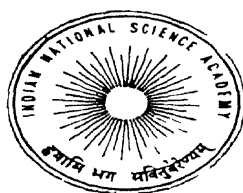
INDIAN NATIONAL SCIENCE ACADEMY NEW DELHI

INSA

ADVANCES IN SOLID STATE CHEMISTRY

**(Proceedings of the INSA Golden Jubilee Symposium on Solid
State Chemistry, New Delhi, December 4–6, 1985)**

Edited By
C N R RAO



INDIAN NATIONAL SCIENCE ACADEMY
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P R E F A C E

SOLID STATE CHEMISTRY is an emerging frontier area of chemical science. The subject is not only academically exciting, but also technologically relevant because of its obvious importance in tailoring solids of desired properties. The Academy considered it most worthwhile to have a symposium on Solid State Chemistry during the Golden Jubilee year. The enthusiastic response from colleagues abroad and co-operation of colleagues in this country has made it possible to organise such a symposium. The participants in the symposium included experts as well as young beginners. There was also a judicious mix of topics covering various aspects of synthesis, structure, properties and reactivity. This volume containing the proceedings of the symposium reflects the present status of the subject and also its interdisciplinary nature.

The symposium had around 50 participants. The small number of participants promoted free exchange of ideas and a cordial atmosphere in the symposium. The symposium owes much of its success to the colleagues from abroad who took considerable trouble to come all the way to India.

I am most thankful to the speakers for providing the manuscripts of their lectures. I do hope that the proceedings will be found useful to all those interested in solid state chemistry.

I am thankful to Dr J. Gopalakrishnan and Mr S. K. Sahní for their invaluable help in organizing the symposium and to Dr M. Dhara and Mr J. Saketharaman in producing this volume.

C N R RAO

President

Indian National Science Academy

Date . 15-03-1986

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Advances in Solid State Chemistry

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DEVELOPMENTS IN SOLID STATE CHEMISTRY : A PARTIAL OVERVIEW*⁺

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(Received 4 December 1985)

A brief survey of recent trends in solid state chemistry is presented. Some of the topics covered are crystal chemistry, synthesis, techniques of characterization, non-stoichiometry, phase transitions, reactions, structure-property relations, non-crystalline solids and catalysts. Several examples from the work carried out in the author's laboratory are cited.

INTRODUCTION

SOLID State Chemistry has emerged to become one of the important interface areas in modern chemical science. We cannot possibly forget that one of the earliest problems that intrigued chemists related to the stoichiometry of chemical compounds in the solid state. This age-old controversy between Berthollet and Proust whether compounds were stoichiometric or non-stoichiometric has been understood relatively recently. The periodic table has formed the basis for many of the advances made in solid state science. It is in efforts to simulate group IV elements like silicon and germanium that a large number of III-V, II-VI, I-VII compounds possessing a variety of electronic properties of technological value were investigated. Intelligent use of the periodic table continues to provide a wealth of ideas for preparing new types of solids possessing novel structures and properties. Solid state chemistry is gaining increasing importance in the last few years because of its role in developing new materials as well as substitutes for natural materials^{1,2}

Chemical science may be considered to have three major components: structure, dynamics and synthesis. These three facets of chemistry also form the essential basis for the contributions that chemists make to the study of solids. The unusual skill with which chemists relate structures of compounds to their properties and synthesize (tailor-make) substances of desired properties makes their contributions to the study of solids unique. Solid state chemistry has, therefore, become an essential part of the broader discipline of materials science with chemists providing their own methods and approaches to the study of solids. In this presentation, I shall briefly survey some recent trends in solid state chemistry^{1,2} in an attempt to illustrate the nature of the subject and to show how it works.

⁺Contribution No. 338 from the Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012.

CRYSTAL CHEMISTRY

Crystal chemistry forms the backbone of much of solid state chemistry. Crystal chemical principles provide the basis for visualising and predicting structures.³⁻⁶ Based on an understanding of the structure and bonding in crystals, one can explain properties of complex solids but and synthesize them. A unique feature of many reactions in solid state is that they are governed by crystal chemistry or packing rather than by the usual rules of chemical reactivity. Although various types of crystal structures have been adequately described in the literature, there have been attempts in recent years to find new ways of describing structures e.g. on basis of reflection, rotation and such operations.^{5,7} The role of non-bonded interactions in determining inorganic structures is being increasingly recognised.⁸ Molecular orbital calculations within the extended Huckel framework are often carried out to explain relative stabilities of structures.^{9,10}

While the structure and lattice energies of common ionic solids can be satisfactorily accounted for within the framework of the Born model, properties of partly covalent solids such as III-V and II-VI compounds can be understood by taking ionicity into account. Phillips' scale of ionicity is eminently useful in this regard.¹¹ Cohesive energies and other properties of organic solids are adequately described by making use of atom-atom potentials, the form due to Kitaigorodskii being especially successful.¹²

Empirical criteria have been derived for the overlap of cation-cation and cation-anion-cation orbitals on the basis of crystal structures to provide a unified picture of magnetic and electronic properties of oxides and other inorganic solids.^{13,14} Conceptual phase diagrams have been constructed in terms of the transfer energy, b , or overlap integral (Fig. 1). A large overlap integral may be due to strong cation-cation or cation-anion-cation interaction; since b depends on the atomic separation, R , the occurrence of a transition from a localized to collective electron behaviour at $b = b_c$ implies existence of a critical distance, R_c , for the transition to occur. One electron energy diagrams are constructed by assuming the most probable hybridization of anionic and cationic orbitals and such diagrams are useful in understanding and predicting electronic and other properties of materials (Fig. 2).

SYNTHESIS

The most common method employed to prepare solids^{3,15-17} is the ceramic method generally involving repeated grinding and heating of reactant powders, many complex oxides are prepared in this manner. Sealed tube reactions are used to prepare chalcogenides. The ceramic method involves large diffusion distances for the reacting cations (upto 100,000Å). Some novel chemical methods of preparing solids have emerged recently and these generally involve low temperatures and often give high surface area products. Of these, the compound or the solid solution precursor method is noteworthy¹⁸⁻²⁰, the method involves forming a compound or solid solution which would contain the required (two or more) cations in the proper

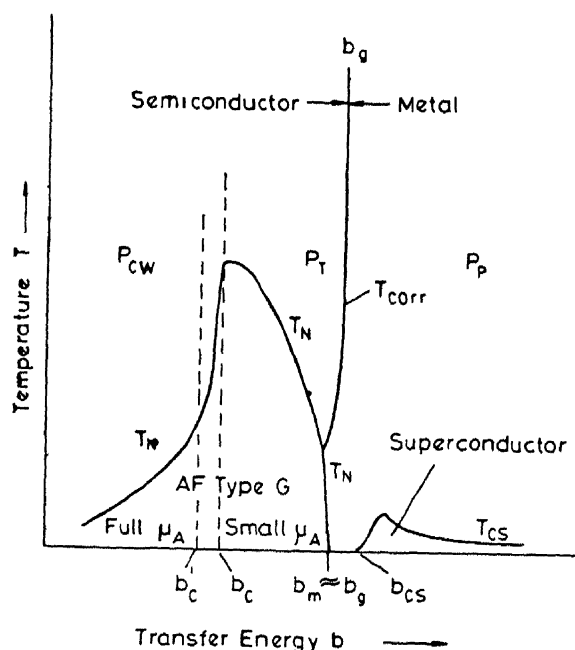


FIG 1 Schematic phase diagram^{13,14}, n_1 is the number of d -electrons per orbital

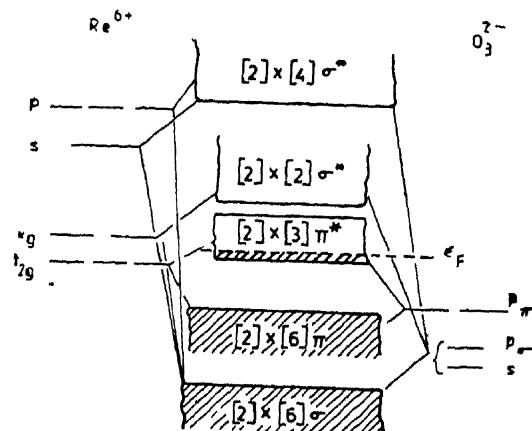
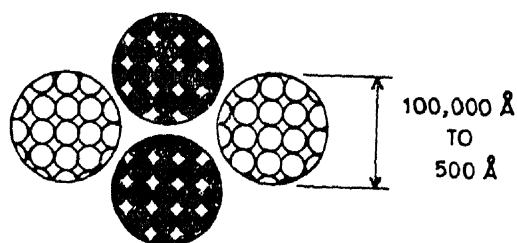
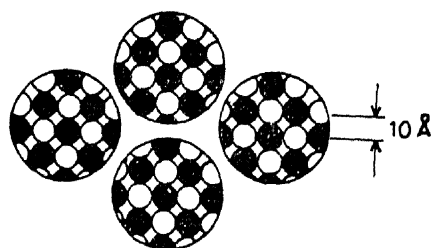


FIG 2 Schematic energy band scheme for ReO_3 ^{13,14}



CERAMIC METHOD



PRECURSOR METHOD

FIG 3 Distribution of different cations in reactant particles and the diffusion distances in (a) the ceramic method and (b) the precursor method

ratio and having an anion lattice that can be readily modified or decomposed (Fig 3). Since the cations are already mixed on an atomic scale (being hardly $10\text{\AA}$ apart) in a single phase precursor, decomposition, oxidation or reduction is

rapid and complete at low temperatures. Compound precursors are not always easy to find for a required preparation. The solid solution method allows a continuous variation of the cation composition. Thus, by employing the carbonate precursor $\text{Ca}_{1-x}\text{Mn}_x\text{CO}_3$, one can make a variety of oxides in the Ca-Mn-O system; there are several other possible carbonate solid solutions of calcite structure formed by Ca, Cd, Mn, Fe and other metals. Unusual oxides such as $\text{Ca}_2\text{Mn}_{2-x}\text{Fe}_x\text{O}_6$ with novel metal coordinations have been prepared from precursors²¹. One can similarly employ nitrate, oxalate, cyanide and hydroxide precursors. Some oxides (e.g. $\text{Pb}_2\text{Ru}_{2-x}\text{Pb}_x^{4+}\text{O}_{7-y}$) can be made by synthesis in alkaline solution.¹⁸ Intercalation, by chemical or electrochemical means, gives oxides such as Li_xCoO_2 , where Li^+ can be reversibly removed.

A number of solids such as transition metal chalcogenides, layered silicates and graphite have been used as host solids to intercalate guest species which vary from atomic species (hydrogen, alkali metals) to molecules (H_2O , NH_3 , heterocyclics, organometallics). The subject of intercalation has grown enormously in the last five years²². The most well-known of the intercalation compounds are the different stage compounds of graphite with electron donor as well as acceptor guests (e.g. K, FeCl_3). Dichalcogenides of group IV, V and VI metals (Ti, Zr, Nb, Ta) possess layer structures which accommodate a variety of guest molecules including Lewis bases (e.g. amines), metal or molecular cations and neutral molecules. These intercalates show lattice expansion perpendicular to the layer planes and some of them exhibit superconductivity.

High pressures are often employed to stabilize high oxidation states of metals or to prepare oxides with a high degree of stoichiometry¹⁵. Hydrothermal conditions are conducive for preparing certain materials including quartz²³. High temperatures often required to prepare refractory materials from melts are achieved by the arc method or the skull method¹⁷. The main point to note is that a broad range of conditions and unique ways of attaining them are available to solid state chemists today, these include irradiation by intense laser beams and electron beams, ultrarapid quenching, very high pressures, carefully controlled oxidising or reducing atmospheres and ultra-high vacuum. Such techniques combined with new methods of characterization have made it possible to prepare an astonishing variety of solids. In the family of metal oxides alone, over twenty homologous series of oxides have been discovered, besides oxides of different structures and controlled stoichiometries, novel suboxides of alkali metals, oxides formed by recurrent intergrowth and with infinitely adaptive structures have been discovered. Chemical vapour transport has provided a means of preparing a number of important materials^{1,17}.

TECHNIQUES OF CHARACTERIZATION

New and improved techniques of characterization that have become available in the last few years have revolutionized solid state chemistry. We shall briefly mention some of the important ones. While X-ray diffraction continues to be an indispensable tool for the determination of structure and identification, high resolution

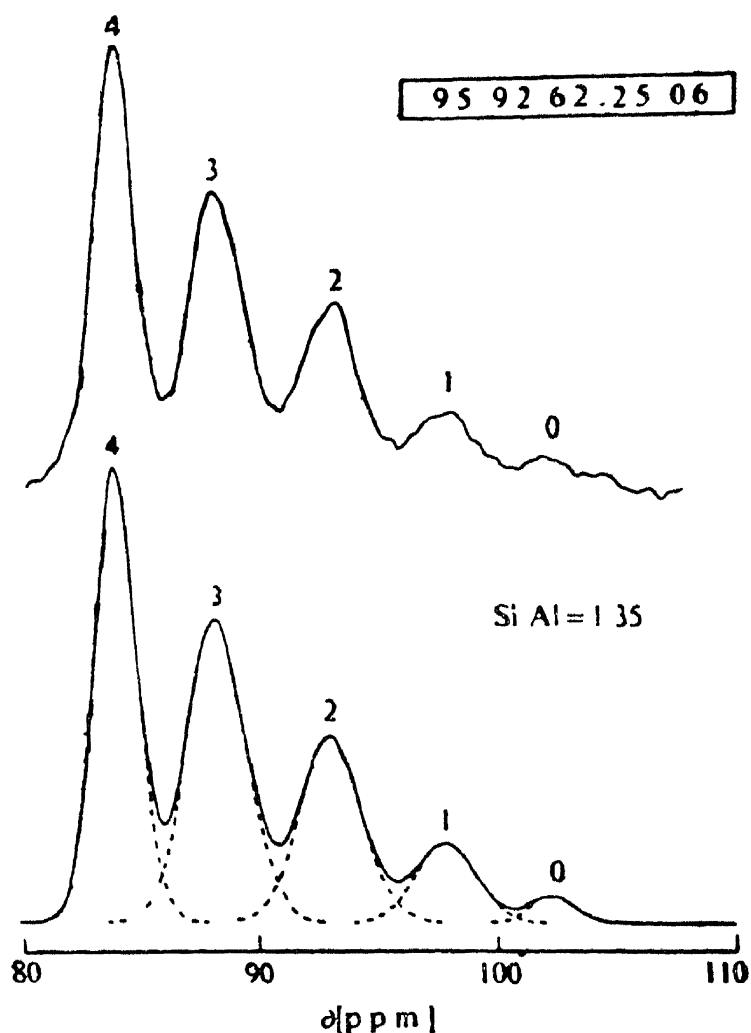


FIG 4 Magic angle spinning ^{29}Si NMR of faujasite. Observed (top) Simulated (bottom). Number shown on peaks are the number of Al atoms surrounding the Si atom ^{26a}

transmission electron microscopy (HREM) has added a new dimension for investigating ultramicro structure and local order of solids, analytical electron microscopy (with EDAX and EELS) can be carried out on as little as 10^{-18} g of the sample $^{24-26}$. Scanning transmission electron microscopy is used to study the morphology of particles (e.g. of catalysts) as small as $10\text{\AA}$. Electron diffraction which is an essential part of HREM provides information on superstructures resulting from defect ordering often not found by X-ray diffraction. Profile analysis of diffraction patterns (both neutron and X-ray) enables the study of structural details even with powder samples. The availability of intense neutron sources has made the neutron diffraction profile analysis ^{27} specially more powerful.

Structural tools such as neutron spectroscopy, optical spectroscopy and Mossbauer spectroscopy are well known ^{2,4,17,23,28} . A recent addition to the arsenal of solid state chemists is high resolution NMR spectroscopy of solids with magic angle spinning and cross polarization ^{29,30} . For example, the ordering of Al and Si

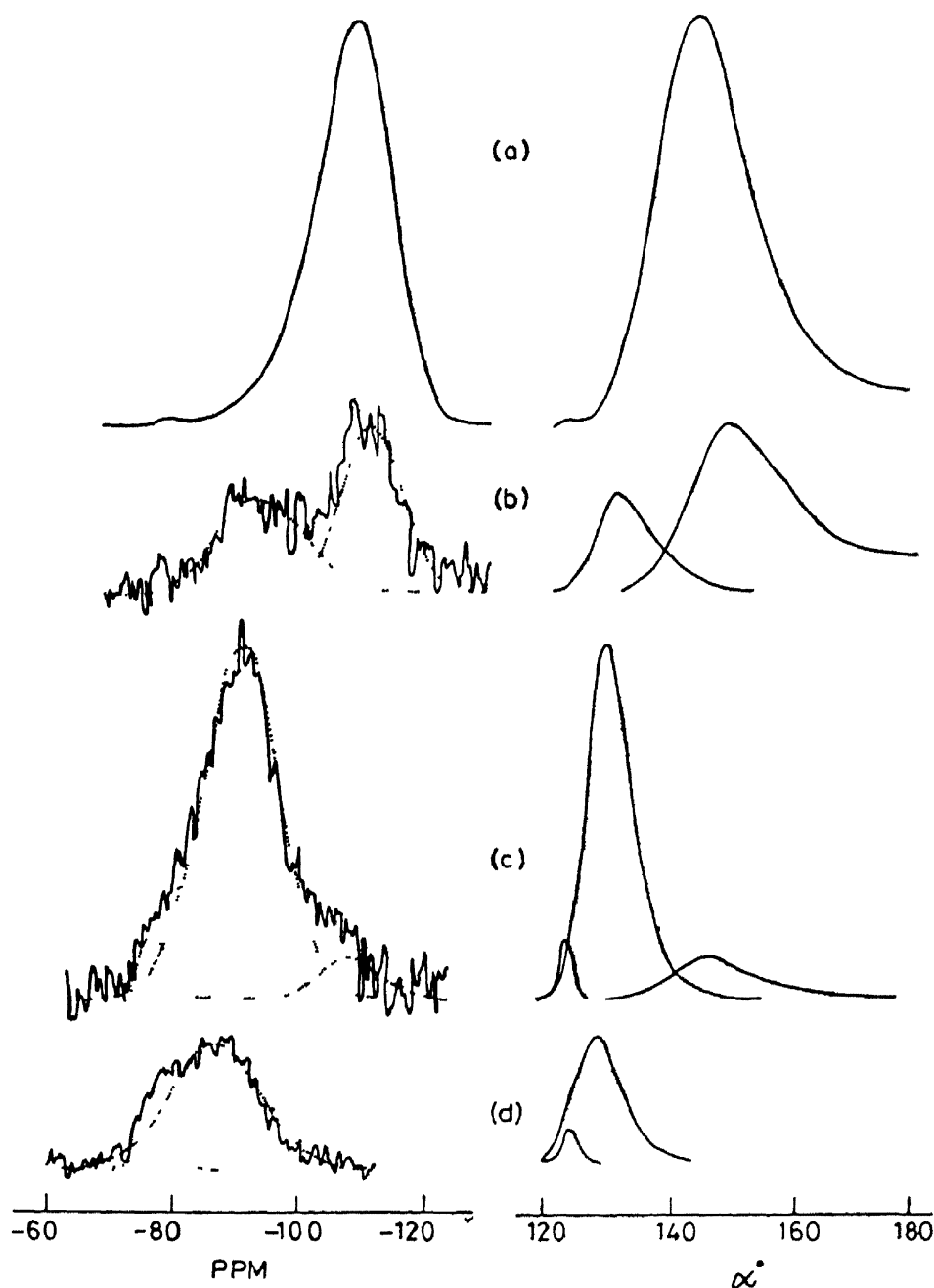


FIG 5 ^{29}Si MASNMR spectra of lithium silicate glasses and their decomposition into Gaussians both in chemical shifts and Si—O—Si angles (α) (a) vitreous silica, (b) $15\text{Li}_2\text{O}-85\text{ SiO}_2$ glass, (c) $33.3\text{Li}_2\text{O}-66.7\text{ SiO}_2$ glass, (d) $40\text{Li}_2\text{O}-60\text{ SiO}_2$ glass³¹

atoms in zeolites can only be found by this technique (Fig 4) and X-ray diffraction is of limited use in this regard. In Fig. 5, we show how the ^{29}Si MASNMR spectra of lithium silicate glasses provide information on the distribution of Si—O—Si angles.³¹

EXAFS, particularly with synchrotron radiation, has been useful to investigate amorphous materials and catalysts.³² In Fig. 6, we give a typical example of the use of EXAFS in the study of catalysts. Surface techniques such as UV and

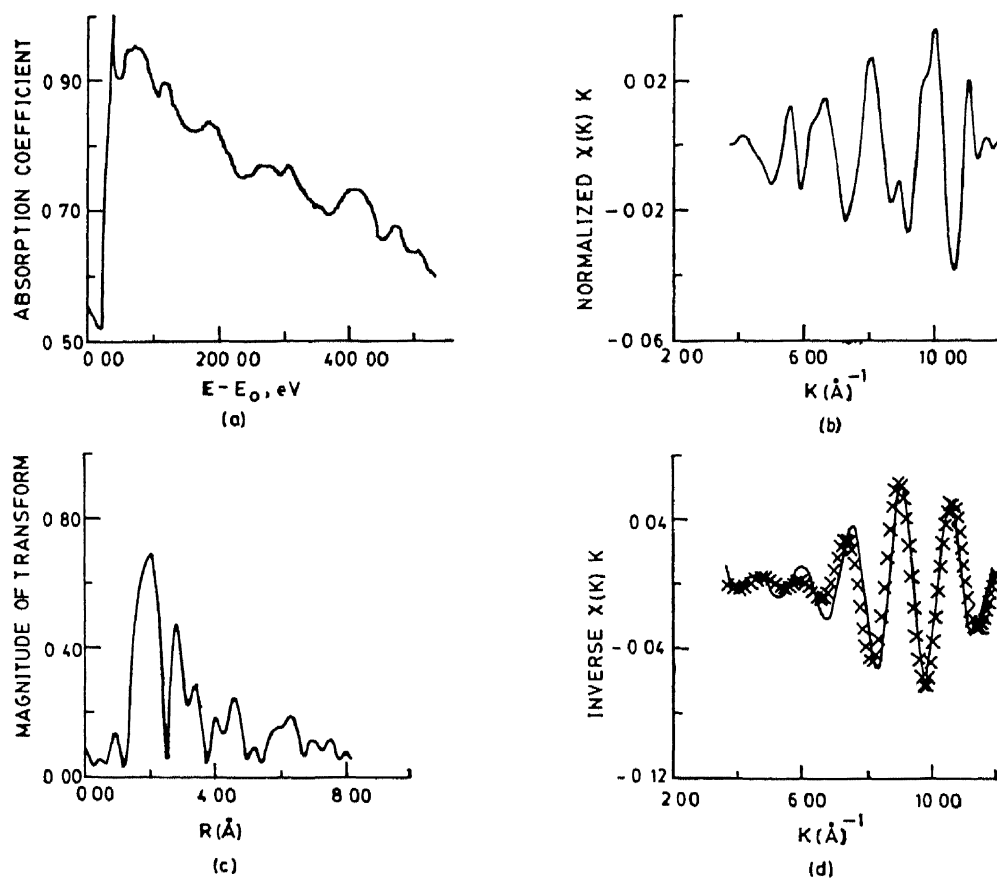


FIG 6 EXAFS study of Cu 75-Ni25/ Al_2O_3 catalyst : (a) Raw EXAFS data, (b) normalized data, (c) Fourier transformed data, (d) back transform and fit to models(after Sankar, Vasudevan and Rao *unpublished results*)

X-ray photoelectron spectroscopy and Auger electron spectroscopy give direct information on the electron states of solids as well as on solid state phenomena^{33, 34} What is truly gratifying today, is the variety of alternative techniques available for investigating solids. For example, the number of *d*-electron states in catalysts and other transition metal systems can be determined by Auger spectroscopy, X-ray absorption spectroscopy (EXAFS and XANES) and electron energy loss spectroscopy carried out in an electron microscope^{24, 35, 36} In Fig 7, we show L edges of three transition metal oxides obtained from EELS carried out in an electron microscope²⁴

DEFECT SOLIDS AND NON-STOICHIOMETRY

Chemists have played a major role in the understanding of point defects in solids from the very beginning, the early contributions of Wagner being particularly noteworthy. Equilibria involving point defects have been usefully investigated from the quasichemical standpoint³⁷ The essentials of the equilibrium treatment involve (a) the intrinsic equilibria of point defects and of electron distribution, (b) the ionization of defects, (c) the transfer reaction whereby atoms of the metal (cation) or the

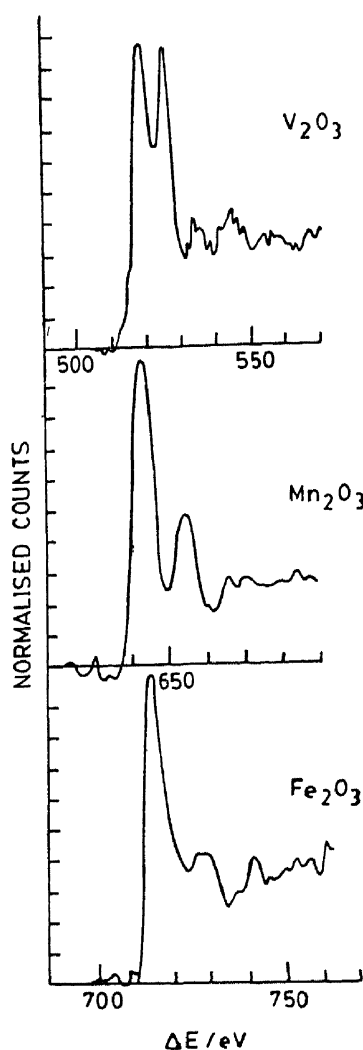


FIG 7 Metal L-absorption edges of three transition metal oxides obtained from EELS carried out in an electron microscope ²⁴

ligand (anion) are exchanged between sites in the crystals and a gaseous phase at a given chemical potential in equilibrium with the crystal and (d) a charge balance condition. It was realized some years ago that all crystalline inorganic compounds have a finite composition range of stability and that it would be more appropriate to talk of the extent of non-stoichiometry in compounds rather than of non-stoichiometric compounds. Although the point defect model provided the basis for discussing non-stoichiometry and contributed much to the advances made in the area of defect solids,³⁸⁻⁴⁰ newer concepts became necessary to understand systems with high defect concentrations^{41,42}

It has now become clear that in systems where deviations in the occupancy of cation and anion sites are large compared to the assigned crystal structure (say 0.1 to 20 per cent sites associated with vacancies or interstitials), the point defect model is not applicable. The real structure of such solids involves complexation or ordering of defects often giving rise to new structural ramifications⁴¹⁻⁴⁶. Thus, in the well-known cation-deficient oxide FeO, defect complexes with four tetrahedral

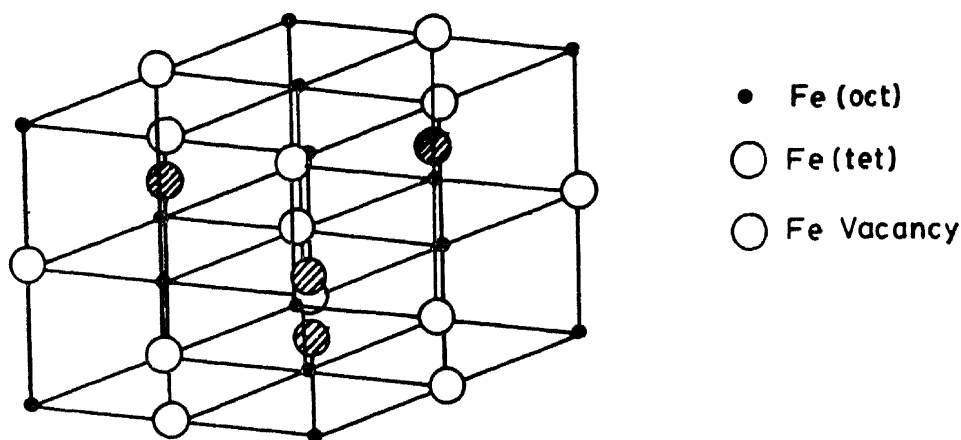


FIG 8 Koch-Cohen cluster in cation-deficient FeO.

iron atoms surrounded by 13 vacant sites (giving the ratio of octahedral cation vacancies to tetrahedral iron of 3:25) are present (Fig 8). Defect complexes are found in anion-deficient oxides of fluorite structure. Such defect clusters are also found in Y_2O_3 -YOF and in ZrO_2 - Y_2O_3 systems. In anion excess fluorites containing high defect concentrations, 2:2:2 clusters are found, a typical example being U_4O_9 . In metallic TiO and NbO (with 15 per cent and 25 per cent of both cations and anions missing), defects are ordered giving rise to low-symmetry structures. Ordering of defects in such solids results in the formation of superstructures readily seen in electron diffraction patterns. A variety of solids show such superstructures including oxide perovskites, metal sulphides and carbides^{42,45}. Computer calculations employing appropriate potentials which were once useful to investigate point defects are employed to study defect ordering as well³⁸.

There are solids where the irrational anion/cation ratios are accommodated by the formation of planar defects or structural singularities. In anion-excess structures, (e.g., YF_3 -YOF), interstitial atoms aggregate into an interstitial disc lying on a crystallographic orientation, the boundary climbing outwards until the singularity extends across the entire cross section of the crystal. In anion-deficient structures, anion vacancies aggregate into a vacancy disc of an appropriate orientation which undergoes a shear displacement until it extends across the crystal⁴⁶. In this arrangement, cation coordination is preserved while the anion coordination is increased, the cation-cation distance is decreased because of the change from corner-sharing to edge-sharing or from edge-sharing to face-sharing of polyhedra. Such planar singularities eliminate a large number of point defects. If deviations from stoichiometry are large, the concentration of planar singularities becomes high and the singularities occur periodically giving rise to ordered phases with finite compositions. Across each planar singularity, slices of the parent structure are in proper register or in an antiphase relation with respect to the cation sublattice, the total composition of the crystal depending on the number of unit cells of the parent structure enclosed between two planar singularities. Creation of a crystallographic shear plane in ReO_3 type structures is shown schematically in Fig 9. It is noteworthy

that even in very slightly reduced TiO_2 ($\text{TiO}_{1.9986}$), a number of shear planes are found, suggesting that even a very small departure from ideal stoichiometry creates shear structures rather than point defects. In the composition range $n = 9-16$ in $\text{Ti}_n\text{O}_{2n-1}$, there is a swinging of shear planes from (132) to (121) through (253), (374), (495) and so on.

In metal oxides derived from Nb_2O_5 , intersecting shear planes occur giving rise to block structures. These structures respond in several ways to changes in metal-oxygen ratios. One shear plane may remain fixed while the other swings, giving rise to different cross-sections of the block, the block getting interconnected in different ways by means of edge- or face-sharing octahedra or tetrahedral sites. Block structures can accommodate a number of distinct compositions, typical ones being $\text{Nb}_{3n}\text{O}_{8n-3}$ and $\text{Nb}_{3n+1}\text{O}_{8n-2}$. Special mention must be made of the continuous series of ordered structures (having apparently irrational shear planes) or the so-called infinitely adaptive structures⁴⁷. Examples of such structures are WO_3 - Ta_2O_5 solid solutions and $\text{Ba}_x(\text{Fe}_2\text{S}_4)_q$.

There are several solids with large unit cells formed by recurrent intergrowth of two phases of similar structure but different compositions²⁵. A typical class of such intergrowths is that of intergrowth tungsten bronzes^{48,49}. An interesting class of intergrowth structures is the barium ferrite system, M_pY_q , where $M = \text{BaFe}_{12}\text{O}_{19}$ and $Y = \text{Ba}_2\text{Me}_2\text{Fe}_{12}\text{O}_{22}$ with $\text{Me} = \text{Zn}, \text{Co}, \text{Ni}$ etc.⁵⁰. Another example is the family of intergrowth oxides of the formula $\text{Bi}_4\text{A}_{m+n-2}\text{B}_{m+n}\text{O}_{4(m+n)+6}$ formed⁵¹ by oxides of the type $\text{Bi}_2\text{A}_{n-1}\text{B}_n\text{O}_{3n+3}$ (Fig. 10). None of the ordered or disordered intergrowth structures shows any evidence of vacancies or other point defects. Ordered and disordered intergrowth structures have been discussed recently⁵². It is truly remarkable that intergrowth structures are formed even though the component units can themselves exist as stable phases.

PHASE TRANSITIONS

A variety of inorganic and organic solids exhibit transformations involving changes in crystal structure or electronic structure. On the basis of crystal chemistry, the nature of structural changes in phase transitions of simple solids can be predicted^{33,44}. Besides nucleation-growth and order-disorder (both positional and orientational) transitions, martensitic transitions have also been observed in many inorganic solids. Polytypism is found in several inorganic solids including perovskite oxides^{44,45}. Of particular interest to chemists are phase transitions involving changes in the spin state of metal ions⁵⁵. Several metal oxides and chalcogenides exhibit metal-insulator transitions induced by temperature, pressure or compositional changes (NiS , V_2O_3 , $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ ^{23,56-58}). The transition in LaCoO_3 at 1200 K is interesting, it is believed that the d -electrons in LaCoO_3 which are localized at lower temperatures become itinerant after this phase transition, the entropy change at the transition being almost entirely electronic in origin. Ag_{1-x}S and other silver chalcogenides become fast ion conductors due to melting of the cation sublattice at the transition temperature. The transitions are also accompanied by marked changes in electronic

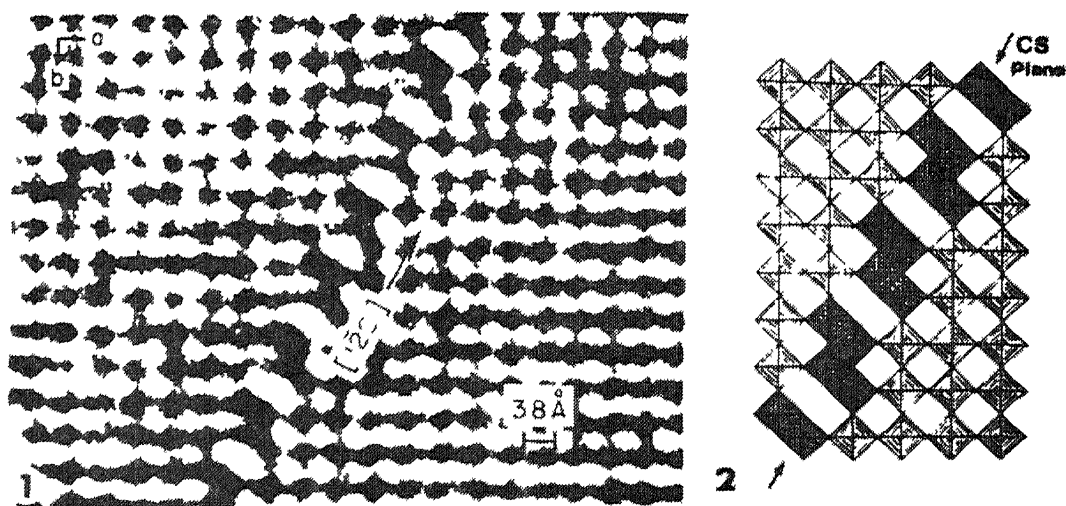


FIG. 9 Crystallographic shear in WO_3 , HREM image (1) and schematic drawing (2) are both shown

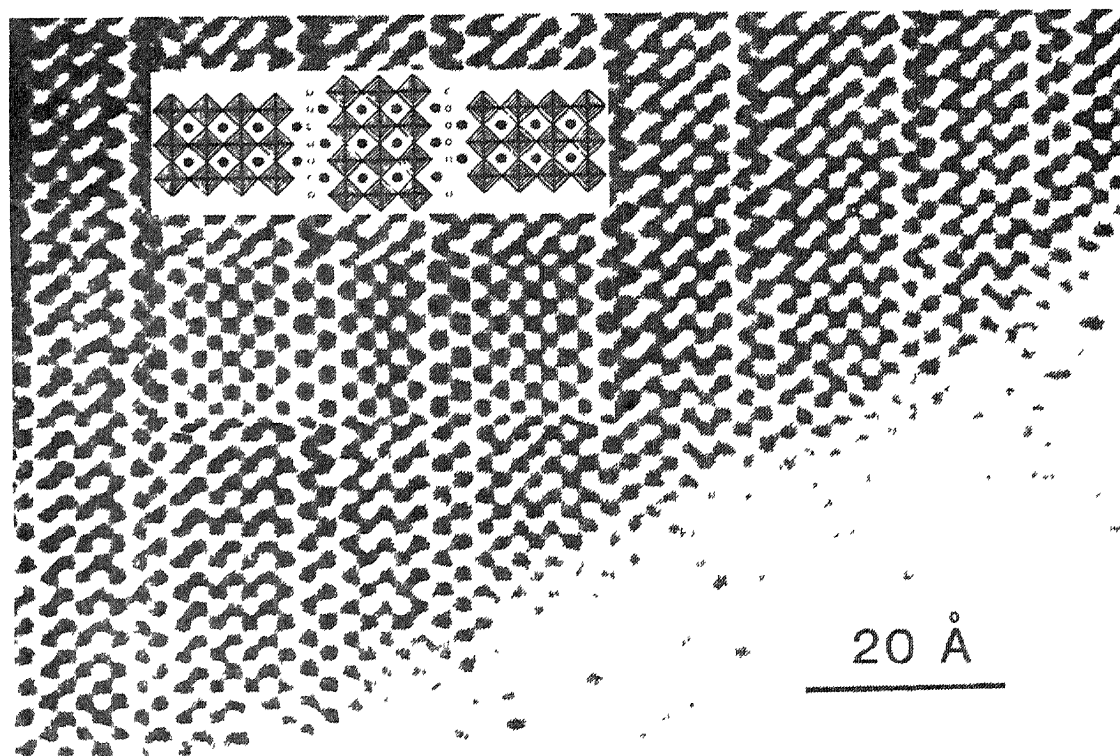


FIG. 10 HRIM image of $\text{Bi}_6\text{Ti}_6\text{CrO}_{25}$ formed by the recurrent intergrowth of $\text{Bi}_4\text{Ti}_4\text{O}_{12}$ and $\text{Bi}_2\text{Ti}_2\text{CrO}_{11}$. Computer-simulated image and structural drawing are also shown.¹¹

conductivity the nature as well as the magnitude of electronic conductivity is crucially controlled by stoichiometry.⁵⁹ A specially interesting metal-insulator transition is that induced by compositional changes (Fig. 11), it is noteworthy that

the value of conductivity at which the temperature coefficient changes sign corresponds to Mott's minimum metallic conductivity.⁶⁰

Organic solids consisting of globular molecules become orientationally disordered (plastic) before they melt, the entropy of the crystal-plastic transition is considerably higher than that of fusion^{61,62} Several techniques are employed to study these transitions

The subject of phase transitions is becoming increasingly an integral part of solid state chemistry and the changes in the physical properties of solids (magnetic, electrical, dielectric etc.) accompanying the transitions are not only of academic interest but also of technological relevance⁵⁴

A specially noteworthy advance made in the last 3 to 4 years is the computer simulation of phase transitions by Monte Carlo and molecular dynamics methods wherein variable-shape, variable-volume simulation cells are employed.^{63,64} In Fig 12 we show the results of a Monte Carlo simulation of the crystal to plastic state transition of CCl_4

A recently recognized variety of phase transitions involves incommensurate structures resulting from two competing periodicities.^{65,66} In conducting solids such as TaSe_2 , interaction between electrons and ion cores occurs at low temperatures rendering the regular array of atoms unstable with respect to certain distortions. The stable state would be one where the charge density, the spin density or ion position exhibits long period modulations. The period of such modulations may be commensurate or incommensurate with the spacing of the underlying lattice. Such-electron phonon coupled structural instabilities are known as charge density waves. Incommensurate structures in insulating solids such as NaNO_2 occur due to the presence of two transformations associated with order parameters of different symmetry. There has been increasing interest in modulated structures in solids.⁶⁷ Phase transitions of these solids and the so-called misfit structures⁶⁸ are undoubtedly of interest.

The origin of long-range-order in polytypes and related solids (e.g. recurrent intergrowth structures) is attracting some attention. The importance of infinite-range interaction and elastic forces has been pointed out^{69,70}, an ANNI-type model is found to explain the occurrence of a variety of polytypes.⁷¹

REACTIONS

A variety of reactions occur in the solid state, decomposition of solids and oxidation and dehydration of solids are typical reactions which have been investigated in detail.¹⁶ Intercalation reactions of solids was referred to earlier. Some solid state reactions exhibit topotactic or topochemical behaviour, typical examples being the oxidation of MnOOH and dehydration of brucite and $\alpha\text{-AlOOH}$. Dehydration of $\text{Mo}_{1-x}\text{W}_x\text{O}_3 \cdot \text{H}_2\text{O}$ to give oxides of ReO_3 structure is another example (Fig 13). Many organic solid state reactions are also known to be topochemical.

Organic solid state reactions, especially those induced photochemically, are indeed interesting.⁷² These reactions are mainly affected by molecular packing

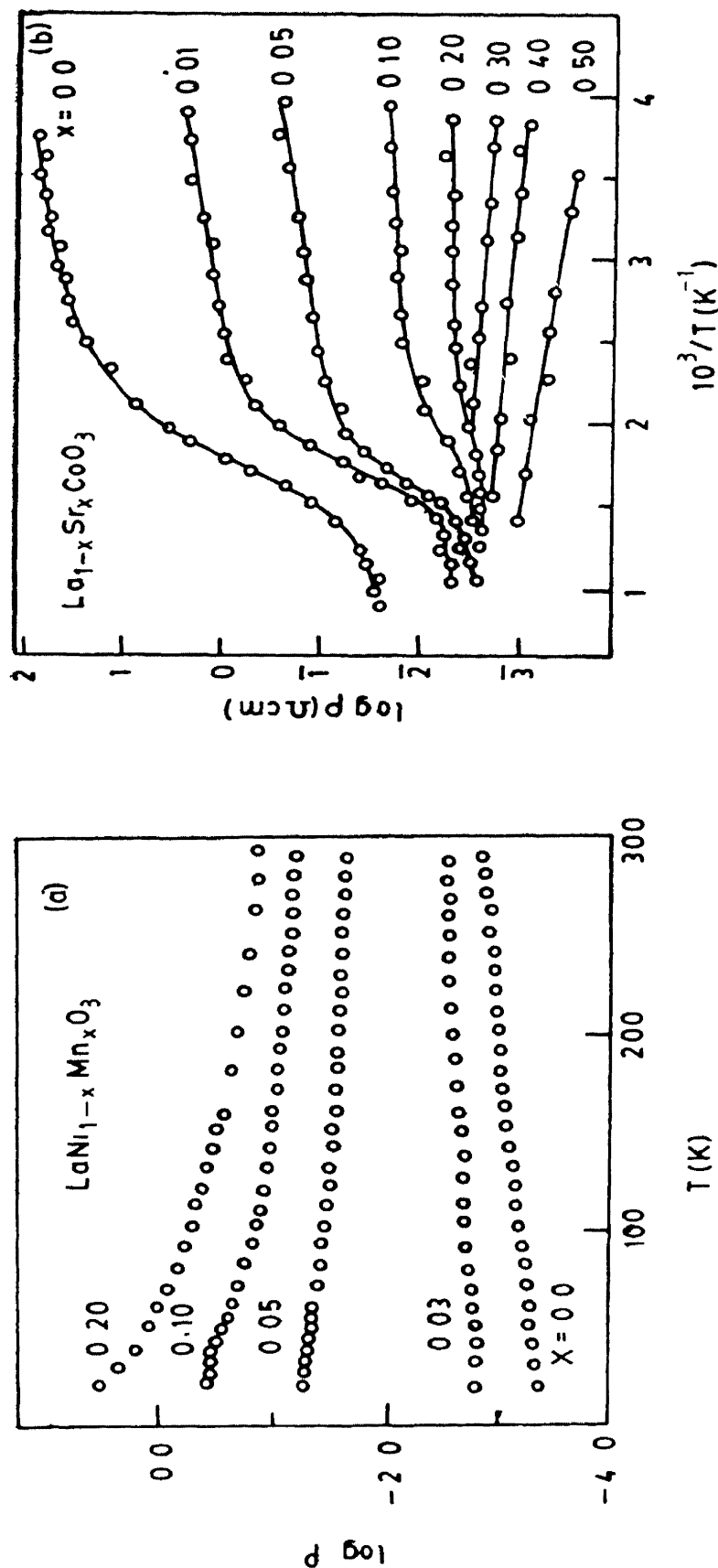


Fig 11 Compositionally induced metal-insulator transitions in $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ and $\text{LaNi}_{1-x}\text{Mn}_x\text{O}_3$ (from the author's laboratory).

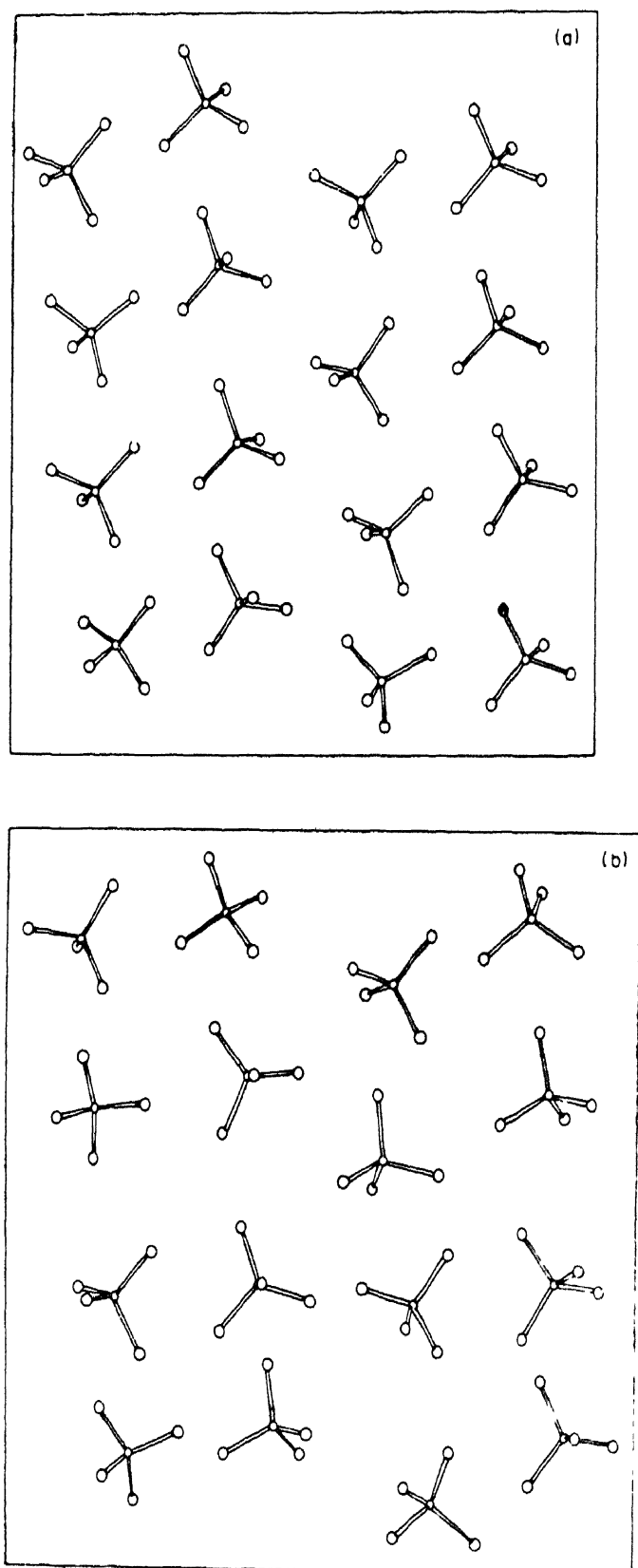


FIG 12 Monte Carlo simulation of CCl_4 at 1 GPa (a) crystalline phase at 380_K, (b) plastic (orientationally disordered) phase at 430 K ⁶⁴

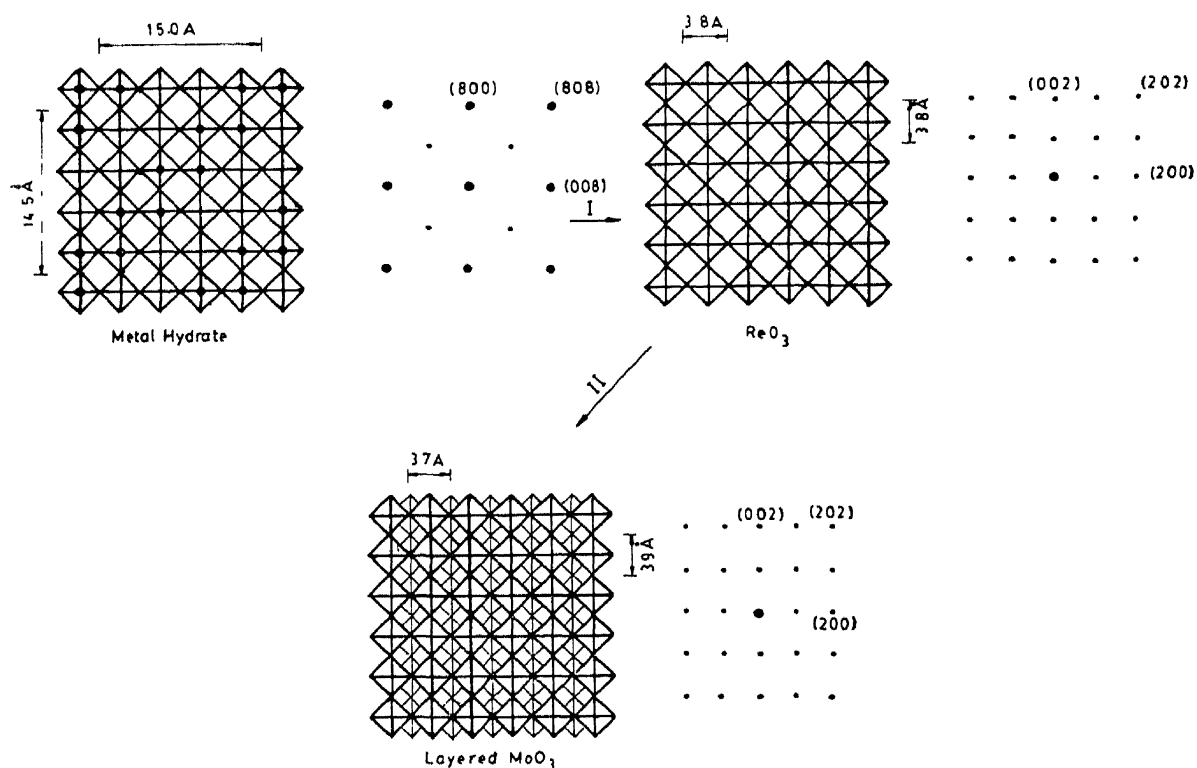


FIG 13 Schematic representation of the topochemical dehydration of the isostructural metal oxyhydrates, $\text{Mo}_{1-x}\text{W}_x\text{O}_3 \cdot \text{H}_2\text{O}$. ($0 < x \leq 1$) along with electron diffraction patterns. Dehydration yields $\text{Mo}_{1-x}\text{W}_x\text{O}_3$ of ReO_3 -type structure. This is true even of $\text{MoO}_3 \cdot \text{H}_2\text{O}$ ($x = 0$), but the ReO_3 structure of MoO_3 is metastable and transforms to the layered MoO_3 structure (*unpublished results from the author's laboratory*)

or by the presence of defects. The classic example of a reaction brought about by the proximity of the reactive centres in a solid is the photodimerization of trans-cinnamic acid where the α -form in which the molecules are packed with a head-to-tail relation yields the centrosymmetric truxillic acid dimer whereas the β -form with molecules packed in head-to-head relation gives the mirror symmetric truxinic acid; the γ -form in which the molecules are not favourably packed is photo-unreactive. Photodimerization of phenylbutadienes⁷³ investigated in this laboratory provides the possibility of a photochromic system, visible light dimerizing the butadiene and UV light reverting the dimer back to the diene (Fig 14). Several types of solid state organic reactions have been described in the recent literature, of particular significance being those directed towards asymmetric synthesis.⁷⁴ It may not be long before the solid state route to organic synthesis comes into vogue on a routine basis (see articles of Jones and Thomas as well as Desiraju in this volume).

STRUCTURE-PROPERTY RELATIONS

Different classes of solids with wide ranges of properties have been investigated by solid state chemists in the last two decades. For example, oxides with metallic, semiconducting or insulator behaviour, ferro-, ferro-, antiferro- or para-magnetic behaviour and ferro-, antiferro- or para-electric behaviour have been explored

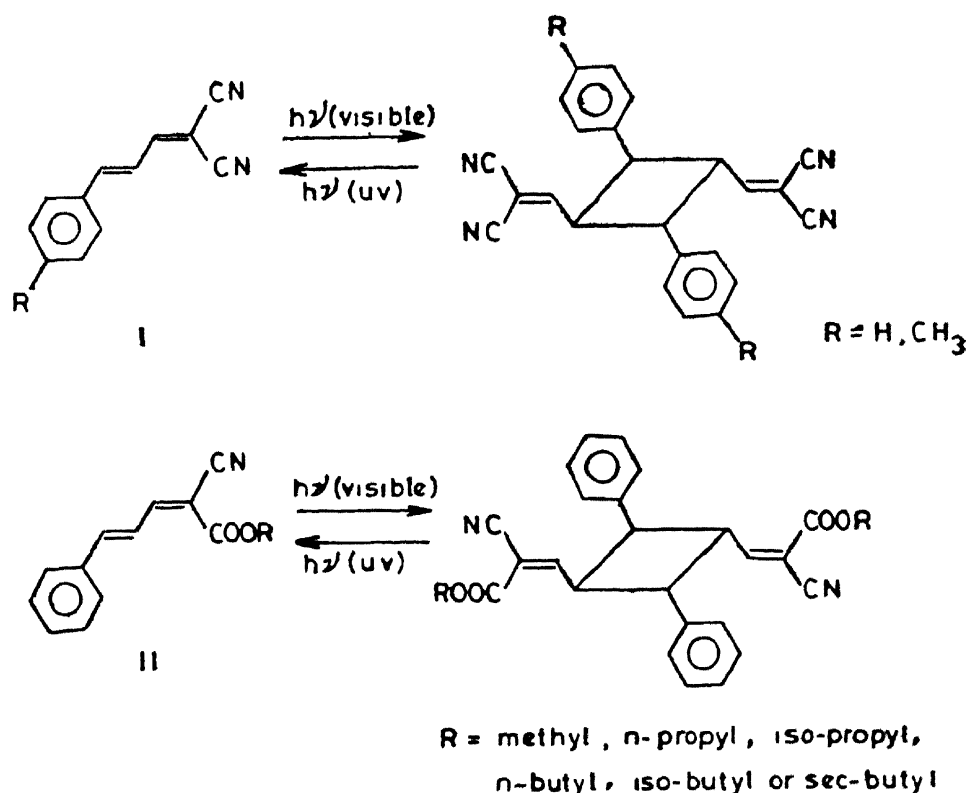


FIG 14 Photodimerization of phenylbutadienes in solid state.

Relating structure and properties of solids and making use of such relations for synthesising novel solids possessing desired properties forms an important mode of investigation of solid state chemists. Simple ion substitution, judiciously carried out, often results in remarkable changes in properties. For example, replacement of La by Sr in LaCoO_3 ⁷⁵ which is ordinarily a paramagnetic insulator results in metallic ferromagnets when the Sr concentration is above a critical value (see Fig 11). Replacement of Si in Si_3N_4 partly by Al and N by O gives a new class of high-temperature ceramic materials called sialon⁷⁶. Pressure effects can often be simulated by appropriate ion substitution, thus, the metal-insulator transition in V_2O_3 is shifted to lower temperatures on substitution of V by Ti (~ 5 per cent) and the effect is similar to that obtained at high pressures. Substitution of V by Cr (< 1 per cent) produces a negative pressure effect. SmS shows a semiconductor-metal transition on application of pressure due to promotion of a $4f$ electron to the conduction band (valence fluctuation). Substitution of Sm by Gd (18 per cent) gives the high pressure metallic phase which on cooling explosively transforms to the semiconducting phase. Design of solid electrolytes (fast ion conductors) for possible application in energy devices is also made on the basis of structural considerations.

Electrical and magnetic properties of low-dimensional solids have attracted much attention in recent years,⁷⁷⁻⁷⁹ some of the motivation resulting from the desire to make high temperature superconductors. Important organic conductors being

investigated are tetrathiofulvalene (TTF)—tetracyano-quinodimethane (TCNQ) and related charge-transfer solids and polyacetylene and related polymeric one-dimensional organic materials. By suitably doping polyacetylene, both *n*- and *p*-type semiconductors can be prepared. Amongst the inorganic one-dimensional conductors, $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3}\cdot 3\text{H}_2\text{O}$ (KCP) and related derivatives and Hg-chain compounds of the type $\text{Hg}_{3-s}\text{AsF}_6$ are noteworthy. Polymeric (SN)_x becomes superconducting at very low temperatures.

Low dimensional solids have been employed as model magnetic systems, solids of K_2NiF_4 structure being typical two-dimensional materials which have been explored extensively. Structure and properties of oxides of K_2NiF_4 structure have been discussed in detail.⁸⁰ La_2NiO_4 has been found to show a metal-insulator transition in the *ab* plane with some evidence for antiferromagnetic ordering in this plane.⁸¹ Low-dimensional solids containing both organic and inorganic groupings have been synthesized.

There is an entire class of materials called the ferroics (Fig. 15) where the orientation state is altered from one to another by application of one or more appropriate forces.⁸² In a ferroelectric like BaTiO_3 , the orientation state of spontaneous electrical polarization can be altered by the application of an electric field while in a ferromagnet such as CrO_2 , the orientation state of spontaneous magnetization in domains is switched by the application of a magnetic field. In a ferroelastic such

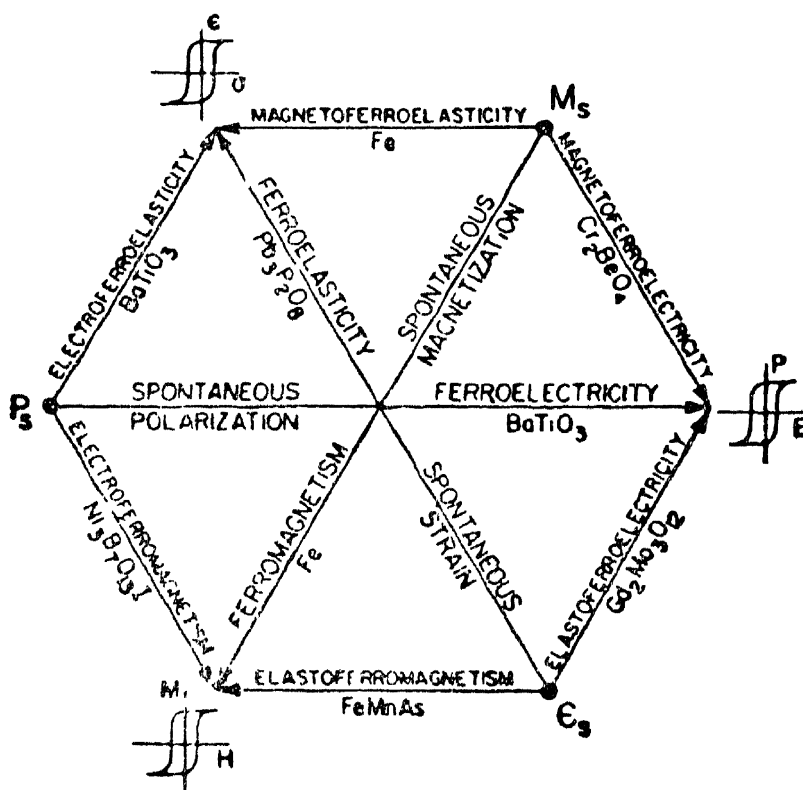


FIG 15 Diagram illustrating various types of order parameters involved in proper and improper ferroics⁸

as $\text{CaAl}_2\text{Si}_2\text{O}_8$ the direction of spontaneous strain in a domain can be switched by the application of mechanical stress. Besides these three primary ferroics, we have secondary ferroics where orientations differ in derivative quantities like dielectric or magnetic susceptibility which characterize the induced effects. Ferroelectric SrTiO_3 , ferrobimagnetic NiO and ferrobielastic SiO_2 are examples of secondary ferroics. Induced effects can also result from cross coupled effects such as stress-induced polarization or magnetization (e.g., piezoelectricity and piezomagnetism). A combined effect of any two types of fields (e.g., elastoelectric or elastomagnetic effects) can also cause induced effects. A novel type of ferroics of technological value is that formed by composites made from ferroelectric ceramics and plastics.

Research in solid state ionics has become a major thrust area in the last few years because of its direct relevance to energy devices. Several materials exhibiting high ionic conductivity and little or no electronic conductivity have been prepared,^{83,84} the oldest example being $\text{Zr}_{0.85}\text{Ca}_{0.15}\text{O}_{1.85}$; this mixed oxide has found several technological applications. Some of the important superionic conductors are AgI related materials such RbAg_4I_5 and β -alumina ($\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$) and its analogues. β -alumina and similar sodium ion conductors could indeed find major applications in the sodium-sulphur battery. Other types of superionic conductors where the mobile ions are protons, Li^+ , Na^+ and F^- have been discovered and there is the expectation that solid state ionics may make an impact through their use in advanced battery systems.

Efforts are underway in many laboratories to explore new systems for ion transport, based on structural considerations, several channel frameworks have been investigated, one of the interesting structures being $\text{Na}_{1+x}\text{Zr}_2\text{P}_{3-x}\text{Si}_x\text{O}_{12}$ (NASICON). Although there has been considerable effort to investigate NASICON related structures, it appears that there is some uncertainty as to the exact composition of NASICON itself. Lithium ion conduction is also being examined for possible use in batteries. An interesting lithium ion conductor discovered recently is the ZrTiI alloy, LiAl . In this connection, the recent discovery of a rechargeable lightweight battery involving LiClO_4 and active carbon (open circuit voltage, 3.9V) is of much interest. A variety of challenging problems are being widely pursued by solid state chemists in the area of batteries and fuel cells. We are yet to find good low-cost oxygen electrodes for use in metal-air batteries and fuel cells, better electrocatalysts are to be found to make this possible. No specific guidelines for the choice of electrocatalysts are available, but high electronic conductivity and oxygen non-stoichiometry seem to be essential. Photoelectrochemical production of hydrogen⁸⁵ poses many problems where solid state chemists are making much contribution. Photovoltaic conversion of solar energy has been a major area of R and D with considerable success and promise.

There are many other classes of important materials with properties of academic as well as technological interest. Mixed valence systems,⁸⁶ liquid crystals and a variety of organic, ceramic and magnetic materials are some of them. For purpose of brevity, we shall not discuss these solids here.

NON CRYSTALLINE STATE

The amorphous state⁸⁷⁻⁸⁹ has been recognized as one of great importance by physicists, electronic engineers and others but chemists seem to have neglected this area at least in the early stages. A large variety of materials of vital importance are amorphous or quasi-crystalline. For example, many of the catalyst preparations involve metals supported on amorphous or partially crystalline substrates while some of the materials used in photovoltaics are amorphous as are the active materials used in reprography and photography. High resolution electron microscopy has been used to delineate ultrastructural characteristics of microcrystalline, partially crystalline and amorphous silica and such studies are useful in providing operational criteria for making such distinctions. It is not possible however, to define a ground state for amorphous materials. Obviously, there can be degrees of amorphousness of a substance and we are yet to find out ways of quantifying the amorphous character of a substance and relate its origin and variations to structure and bonding. EXAFS and XANES have been used extensively to investigate structures of amorphous materials, but these techniques are not entirely fool-proof or always successful.

Most substances can be made amorphous by quenching melts or depositing vapours. Two important characteristics of the amorphous state are freedom from order and from compositional restrictions. Compositions of amorphous materials are continuously variable, because of this property, there is local saturation of valence requirements in covalently bonded solids or creation of structural groupings which achieve electrical neutrality in ionic systems. Amorphous materials exhibit unique electronic and other properties, some of which are of potential technological value. Glasses are amorphous but are distinct from other amorphous materials by virtue of the glass transition they exhibit. Although glasses are supposed to be in a metastable state, they exist as stable materials for indefinite periods. For example, vitreous carbon is employed in high temperature applications, crystallization of vitreous B_2O_3 is possible only under severe conditions.

In the last decade, there has been considerable activity in the area of amorphous solids in order to explore the physical laws that govern the behaviour of non-crystalline solids as well as to prepare new amorphous materials with controlled properties. A variety of amorphous solids including metallic glasses have been prepared. The quenching rates attainable today in melt-quenching techniques are of the order of 10^6 – 10^7 deg sec⁻¹. We have available today, glasses with transparency in any region of the electromagnetic spectrum, glasses which are semiconducting or ferroelectric, glasses with controlled magnetic properties and so on. A great advantage of amorphous (and glassy) materials is the ease of fabrication.

The unique phenomenon of the glass transition⁹⁰ exhibited by glasses is a transition from one metastable, non-crystalline, rigid state to another metastable, non-crystalline, but non-rigid state characterized by features of pseudo second-order transitions. However, there is no totally satisfactory model or theory for this phenomenon. Some workers attach significance to a thermodynamic transition

temperature, T_0 , where dynamic rates vanish, but this approach does not explain all the known properties of glasses. Results from computer simulation studies reveal the formation of clusters in supercooled liquids prior to glass transition. The glass transition could then be a congelation of these clusters. Clusters of 500–100 Å diameter present in the non-crystalline intercluster tissue material of lower density, melt at the glass transition and add on to the volume of the tissue material. The recent Monte Carlo study of the glass transition in isopentane⁶⁴ has revealed the importance of geometric factors; the study depicts differences in packing and structure between the liquid and the glassy states.

A remarkable feature of amorphous solids governed by the chemistry of these materials is the occurrence of novel chemical transformations and structural rearrangements on an atomic scale. Thus, a continuous variation of the concentration of tetrahedral and planar (3-coordinated) borons is achieved in borate glasses by modifier oxides. Both over- and under-coordinated, charged chalcogen (or pnictogen) defect centres present in chalcogenide (and pnictide) glasses play a crucial role in transport and related properties. These charged pairs result from a favourable reaction of bonds which initially suffer homopolar scission. Oxygen coordination of germanium varies as a function of the modifier oxide in germania glass, varying from four to six and to four again in modifier oxide rich regions.

The nature of bonding in amorphous materials provides new challenges. As mentioned earlier, an important characteristic of the amorphous state is the presence of both compositional and density fluctuations, these fluctuations are accompanied by fluctuations in the nature of bonding. Most of the common multi-component oxide glasses consists of both charged ionically bonded oxygens and two-coordinated covalently bonded oxygens, their relative proportions being continuously variable. Chalcogenide glasses (e.g. As_2Se_3 — As_2Te_3) are cases where both ionic and covalent bonds are present between similar sets of atoms.

A significant development in glasses is the observation of fast ion conduction^{90a}. A variety of fast ion conducting glasses based on Ag^+ and Li^+ ions have been characterized. Besides the ease of fabrication, glassy fast ion conductors offer advantages of property manipulation through composition control. The field of optical communication is based on the development of glass fibres with controlled optical properties. A unique property of the glassy state is that the refractive index is determined by the chemistry of the glassy state, halide glasses offer tremendous possibilities in this direction. Unusual photostructural effects have been found in amorphous WSe_2 and other systems and it is of much interest to find out the cause of such effects and also their possible applications.

Recent studies⁹⁰ have shown that one can generate orientationally disordered glasses by quenching plastic crystals, these glasses also show a glass transition. Dipoles doped in ionic crystals (so called dipolar glasses) are also found to show a glass transition. These systems are indeed most interesting and show how the glass transition is not a property of positionally disordered glasses alone.

Recently, quasicrystalline alloys (e.g. Al-14 percent Mn) prepared by rapid solidification of melts have been found to exhibit three-dimensional icosahedral

point symmetry^{91,92} or Penrose patterns. This was considered to be a revolution in crystallography, but Pauling's idea⁹³ based on chemical considerations suggest twinning of cubic crystals may be an important factor, but features such as the electron diffraction patterns are yet to be explained.

CATALYSTS

Modern chemical industry depends heavily on the development of appropriate catalysts. The performance of catalysts depends both on their solid state (bulk) and surface properties. Molybdate catalysts for olefin oxidation and ammoxidation reactions and shape-selective zeolites for various purposes (especially in petroleum industry, e.g. ZSM-5 for methanol to gasoline conversion) are typical examples of the new generation of catalysts. Design of shape-selective catalysts wherein the pore aperture and diffusion path lengths are finely engineered is an important aspect of catalyst development. Better catalysts are required for many reactions such as ammonia synthesis, hydrocarbon oxidation, methanol synthesis and for (Ziegler-Natta type) stereospecific reactions. It may be possible to use oxide catalysts such as defect perovskite oxides, supported V_2O_5 or molybdates for hydrocarbon oxidation, just as defective Cu/ZnO may be useful for methanol synthesis. Search for newer and better catalysts will undoubtedly continue. With the availability of new and improved techniques for the characterisation of the bulk and surface properties of solids, it is expected that the art of catalysis may soon become a science. Catalysts are accordingly included under solid state chemistry and materials science in recent years⁹⁴. For example, the surface species on Co-Mo hydrodesulphurization catalysts is recently found to be of the type $CoMo_{2n}(2n+3)S_2^{2-} - (2n-2)S^{2-}$, involving disulphide ions, this has been possible because of the use of X-ray photoelectron spectroscopy and X-ray absorption spectroscopy⁹⁵. Besides photoelectron spectroscopy and related surface techniques, techniques such as NMR spectroscopy^{29,96}, EXAFS³² (see Fig. 6) and other techniques have proved to be a boon to the study of catalysts, FTIR spectroscopy seems to be ideally suited for study of molecular species on catalyst surfaces, especially when it is used in the reflection-absorption mode along with photoacoustic detection.

Metal cluster compounds containing metal aggregates surrounded by ligands provide model systems which simulate surface species produced by the interaction of molecules with metal surfaces^{97,98}. Metal clusters may be considered to fall in the range of aggregation between single, mononuclear complexes and macroscopic crystallites, the latter including supported metal catalysts (e.g. Pt/ Al_2O_3) which generally consist of aggregates of metal atoms (crystallites) bonded to an inert support. The support also contributes to catalytic effects in certain systems (e.g. Pt/ TiO_2).

Metal cluster compounds are a combined outcome of efforts in organometallic chemistry, surface science, heterogeneous catalysis and allied fields. The development of selective catalysts for the C_1 chemical industry employing carbon monoxide (or possibly CO_2) as the raw material has resulted in major efforts in metal cluster research. The interest of solid state chemists and surface chemists in this area

arises from the close correspondence between metal cluster compounds and the metal crystallites on surfaces of supported metal catalysts as well as the surface species formed by molecules on catalyst (or metal) surfaces.

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ADVANCED PHYSICAL METHODS FOR THE CHARACTERISATION OF POWDERS

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A wide range of physical methods is now available for the study of powder materials. Recent advances in some of these methods, including analytical electron microscopy, magic angle spinning NMR, and powder diffraction with X-ray and neutrons, are described, and the scope and limitations of the techniques are discussed.

Key Words : Physical Methods; Electron Microscope; Magic Angle Spinning NMR; Powder Diffraction with X-rays and Neutrons

1 INTRODUCTION

THE need for new materials for a wide range of applications, including catalysis, energy storage, and solar conversion, is widely recognised,¹ but it is probably true that our ability to prepare such materials now exceeds our ability to characterise them. Most new materials that reach the stage of commercial application will be used in the form of powders, but in many cases the initial characterisation has been carried out by using single crystals. Typically, this vital step involves a definitive structure determination by X-ray diffraction. For materials that can only be made in powder form, however, the route to complete characterisation is more precarious. Traditionally, X-ray powder diffraction will be used to identify a new phase, but if the pattern is complex, it may be difficult to index it and determine the crystal system and lattice parameters. Under these circumstances, very careful work is required even to confirm that the material is a single phase, and it is not unusual for the composition, determined by bulk chemical analysis, to be incorrectly assigned. Even if the X-ray pattern can be indexed, problems can still arise. To take a recent example, the composition of the sodium conductor NASICON, which was first reported in 1976,² has been the subject of a great deal of discussion.³ In instances where the powder pattern cannot be indexed, the likelihood of obtaining a full structure is remote, and in many cases this will preclude further development of the material. For example, the potential of a new zeolitic material for shape-selective catalysis is determined almost entirely by its structure, and it is clearly a great disadvantage if this is unknown. In order to take full advantage of the many exciting developments in synthetic chemistry, it is therefore essential that proper attention should be paid to the improvement of physical methods.

The purpose of this paper is to describe some of the advanced methods that are now available for the characterisation of powders. In the last decade, substantial progress has taken place in many areas. Analytical electron microscopy offers the possibility of determining the compositions of the constituent phases in even the most complex mixture⁴. High resolution powder diffraction methods, especially using neutrons, are now able to solve structures *ab initio*⁵, and magic-angle spinning techniques have brought the power of nuclear magnetic resonance to the solid state⁶. These, and other methods that can be applied to the study of powders, are discussed in the following sections.

2 ANALYTICAL ELECTRON MICROSCOPY

2.1 Introduction

The first step in the characterisation of a powder sample is the determination of the composition of the phase or phases that are present, and it is here that the analytical electron microscope can play a unique role. A modern transmission electron microscope is a very versatile instrument, offering a wide range of modes in addition to diffraction and imaging. These can best be understood by examining some of the many ways in which the electron beam can interact with the specimen (Fig. 1). The modes that are of particular relevance to the study of powders are reviewed in the following sections.

Transmission Electron Microscopy (TEM, diffraction) Electrons are normally generated by thermionic emission from a cathode filament, often tungsten, and monochromated by acceleration through a potential, E . For an accelerating voltage

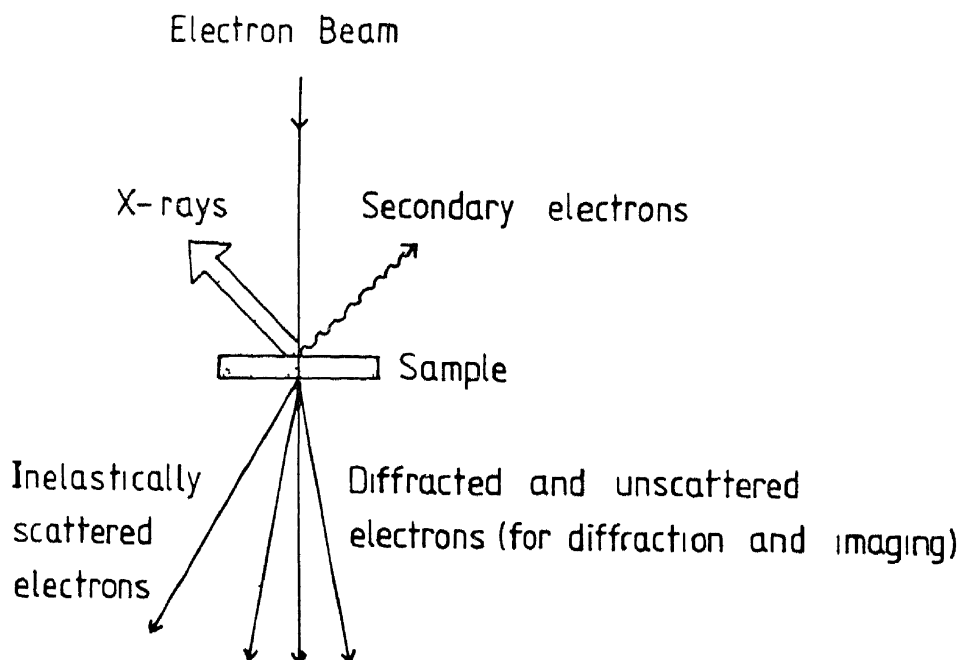


FIG 1 Some of the important interactions between an electron beam and a specimen

of 100keV, the wavelength is 0.037Å. Electrons may be elastically scattered by the atomic potentials of the atoms in the specimen, leading to the formation of a diffraction pattern for a selected area of crystalline material. This can provide useful information concerning the lattice parameters and crystal system of the material. The diffraction pattern may, in turn, be transformed by a magnetic lens into an image of the specimen, a step that requires human intervention and a great deal of computing with X-rays. The use of high resolution electron microscopy to obtain images with atomic resolution will be discussed in a later section.

Scanning Electron Microscopy (SEM, STEM): The low energy electrons (less than 50eV) that are emitted from the surface of the specimen during electron irradiation form the basis for a different type of imaging. The beam may be concentrated to a small probe (say 20Å diameter) that can be deflected across the specimen in a faster fashion using scanning coils. The secondary electrons can be detected above the specimen, and an image showing the intensity of secondary electrons emitted from different parts of the specimen surface can be displayed on a CRT. This SEM mode is particularly useful for examining the morphology of a crystal surface.

A related technique involves the collection of electrons that are transmitted through the specimen during scanning. These can be used to produce a scanning transmission (STEM) image, with the advantage, compared with TEM, that radiation damage is reduced because the beam is not stationary.

X-ray Emission Spectroscopy: One of the most important interactions between the electron beam and the specimen is the stimulation of characteristic X-ray emissions from the elements present. These can be detected and sorted into different energies by using a crystal monochromator or an energy dispersive detector. X-ray detection has been used for many years on scanning microscopes (the microprobe), but only recently has it found widespread use on transmission instruments. The resulting spectra (see Fig. 2) are extremely valuable for chemical analysis of powders.

The intensities of the spectral lines can be related quantitatively to the composition of the sample. For thick specimens (the usual microprobe situation)

$$C(x) = k Z A F I(x), \quad (1)$$

where $C(x)$ is the concentration of element x , k is a constant, Z is an atomic number correction, A is an absorption correction, F is a fluorescence correction, and $I(x)$ is the intensity of a characteristic X-ray emission of x .

For thin specimens (the typical TEM situation)

$$\frac{C(x)}{C(y)} = k_{xy} \frac{I(x)}{I(y)} \quad (2)$$

The method requires a standard compound in order to determine the value of k_{xy} , but once this has been established for a particular pair of elements (on a given

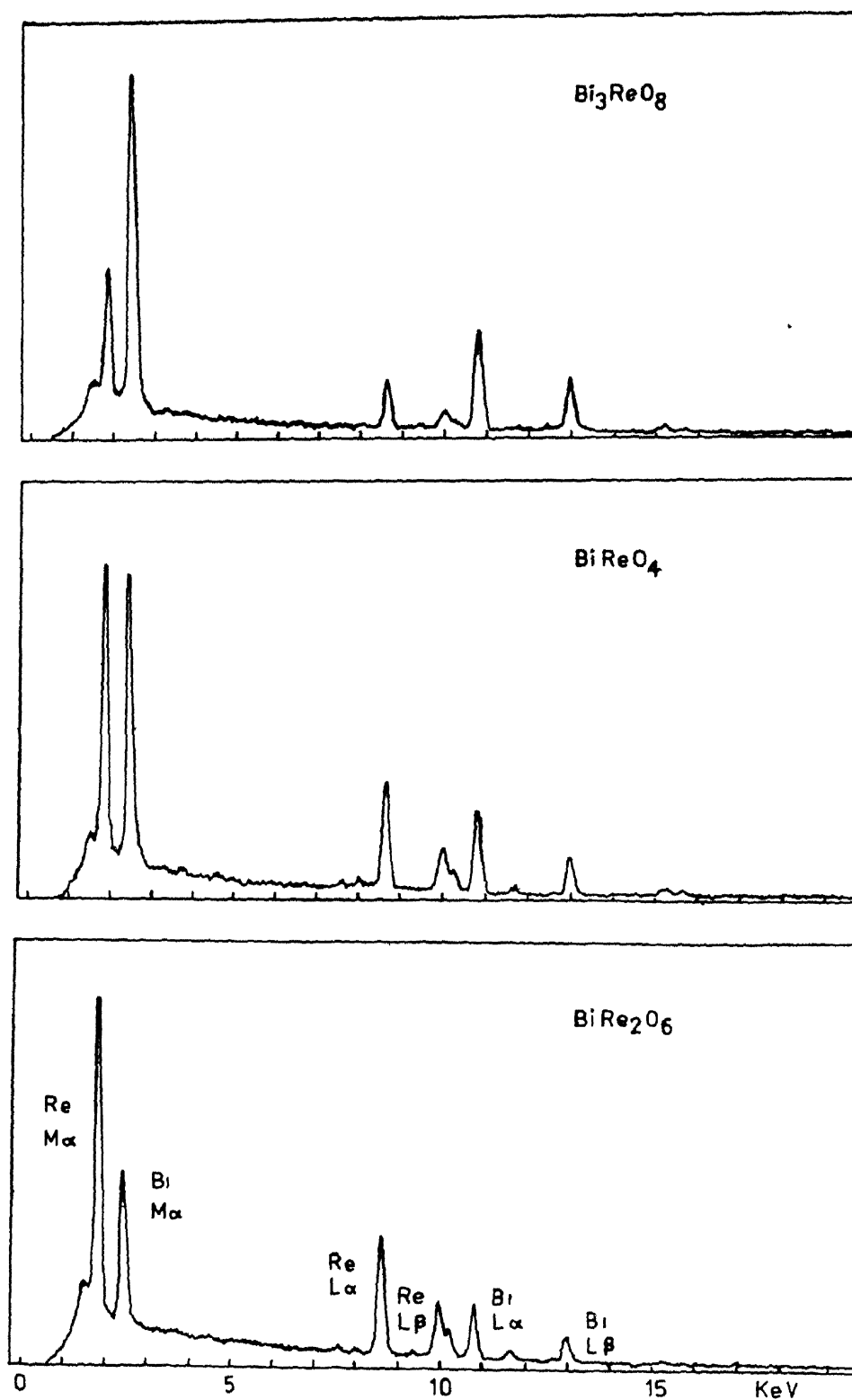


FIG 2 X-ray emission spectra obtained from thin crystals of Bi_3ReO_8 , BiReO_4 , and BiRe_2O_6 at 100 KeV on a Jeol 100CX TEMSCAN instrument.⁸ The Cu lines arise from the supporting grid

instrument), the same value can normally be used for any other compound containing those elements.

Electron Energy Loss Spectroscopy (EELS): Energy loss spectroscopy looks at inelastically scattered electrons that have lost energy in the sample due to a range of processes, including plasmon excitations and the ionisation of core electrons; the latter is the preliminary step in X-ray emission. A typical spectrum is shown in Fig. 3. The sharp peaks on the L-edge of vanadium stem from electric dipole transitions between the $2p$ and $3d$ levels. It has been shown that the ratio of the intensities of these peaks is a function of the number of d electrons, and therefore the oxidation state⁷. The position of the edge is also affected by the oxidation state.

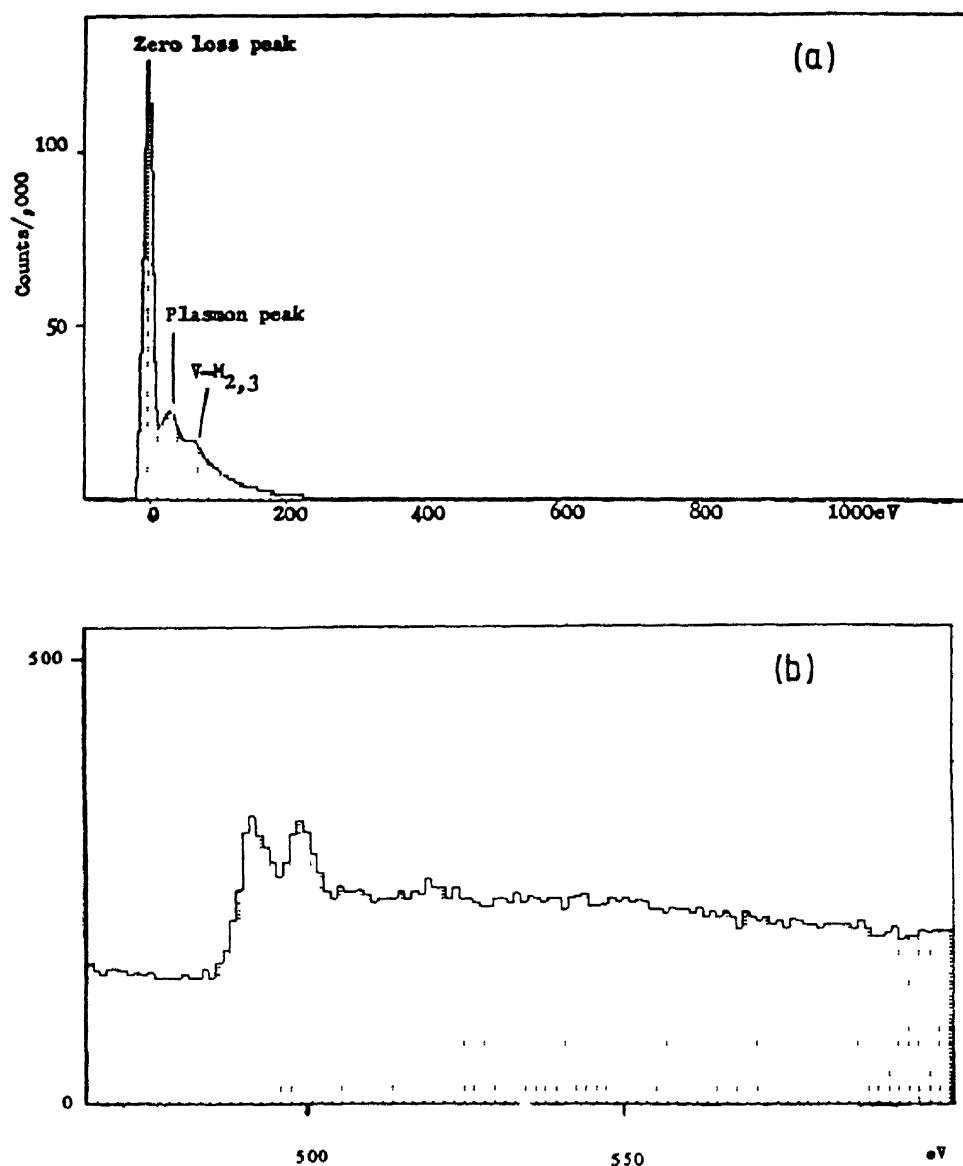


FIG 3 Electron energy loss spectra of a vanadium oxide, obtained at 200KeV on a Jeol 2000FX TEMSCAN instrument—

(a) Full spectrum, 0–1100eV range

(b) Detail at the vanadium L-edge, showing the L_{2,3} fine structure (Cheetham and Starr, unpublished)

The EELS method is the most sensitive in the 0–1000eV range, a range that includes the K-edges of the elements H-F, and is therefore useful for analysing light elements that are not always detected in X-ray emission spectroscopy. Elemental maps may also be obtained in the form of energy filtered images.

2.2 Applications

The applications of analytical microscopy in solid state chemistry have been reviewed by Cheetham and Skarnulis⁴. The major advantage is that chemical compositions can be determined with very high spatial resolution by utilising the magnifying power of the instrument. This permits the compositions of the phases that make up a complex mixture to be examined individually, thus facilitating phase identification. An important area of use is in synthesis, where the traditional approach of powder X-ray diffraction, though invaluable in many instances, can be rather uninformative if the patterns of the product phases are entirely new. The electron microscope enables us to probe the compositions of the phases, directly. For example, in a study of the system Bi–Re–O, Rae-Smith and Cheetham⁸ were able to identify three new compounds in the product of a single reaction between Bi_2O_3 and ReO_3 : Bi_3ReO_8 , BiRe_2O_6 , and BiReO_4 . The X-ray emission spectra are shown in Fig. 2. Note that in this case, the Bi/Re atomic ratio of each phase can be deduced by simple inspection of the Bi(M)/Re(M) intensity ratio. The methodology is to identify the compositions of the compounds present in the mixture and then to prepare each one in a pure form for further characterisation. Another area of use is in the elucidation of phase diagrams, where the tie-lines can be constructed from the compositions of the phases that are in equilibrium. A simple illustration is the use of AEM to establish the mutual solubilities of FeS_2 and MnS_2 in the solid state⁹.

A close inspection of Fig. 2 reveals that the X-ray emission spectra do not yield the compositions of the new oxides without ambiguity, since the oxygen K line cannot be observed due to absorption by the detector window. It is typically the case that the emissions from elements lighter than sodium ($i.e. < 1\text{Kev}$) will be unobserved. In the Bi–Re oxides, therefore, only the Bi/Re ratios could be determined, and other information was required in order to complete the analysis. BiReO_4 and $\text{Bi}_3\text{Re}_3\text{O}_{11}$, for example, give indistinguishable X-ray spectra¹⁰. Recently, a new type of thin window X-ray detector, which extends the elemental range down to carbon, has become available, and the early indications are that quantitative oxygen analysis should be possible with such devices^{11,12}. Fig. 4 shows a typical spectrum obtained with a thin window detector, and Fig. 5 confirms that metal/oxygen ratios can be obtained by using the thin crystal approximation.

An alternative approach to light element analysis involves electron energy loss spectroscopy. Loss peaks from the first row elements, Li–Ne, fall in the most sensitive part of the EELS spectrum, between 0 and 1000eV, and quantitative metal/oxygen ratios have been obtained by measuring the areas under the appropriate edges¹³. More directly, it may be feasible to assign the oxidation state of, say, a transition

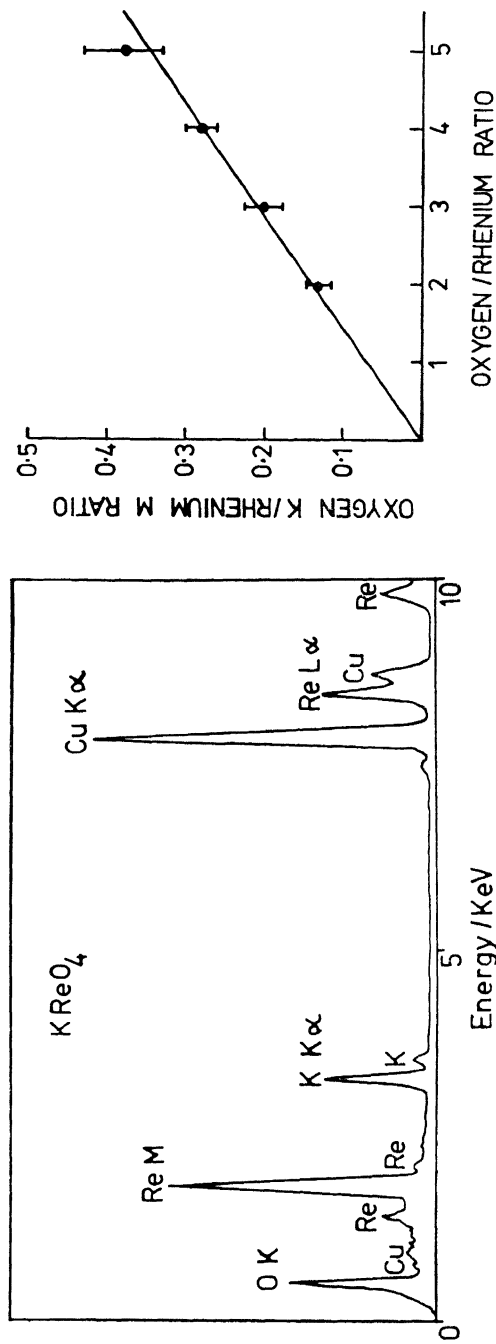


Fig 4 X-ray emission spectrum of KReO_4 , obtained at 200 KeV on a Jeol 2000EX TEMSCAN instrument equipped with a Tracor thin-window detector¹²

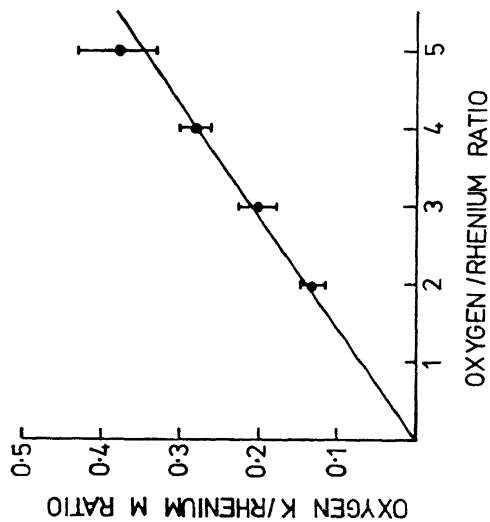


Fig 5 Oxygen K. Rhenium M intensity ratios, plotted versus oxygen-rhenium atomic ratios for a series of oxides. ReO_3 , ReO_4 , KReO_4 and Ba_2ReO_5 ¹² The linearity of the results confirms that quantitative oxygen analysis can be obtained with thin crystals, according to equation (2).

metal by a careful study of its EELS peak. This has been attempted in two ways. First, the edge itself may exhibit a shift that depends upon oxidation state. For example, Rao *et al* have shown that the L -edge of manganese, which corresponds to the ionisation of a $2s$ electron, varies smoothly in a series of binary and ternary oxides¹⁴. Second, the sensitivity of the L_3/L_2 intensity ratio to the number of d -electrons, which was described above, can, in principle, be used to determine oxidation states.

The power and versatility of AEM has already been demonstrated, but a great deal of potential still remains to be tapped. The EELS technique is only just beginning to make its mark on chemistry, and future developments in instrumentation and data processing are likely to enhance its capabilities in several ways. Particular attention will focus on the information content of the near-edge fine structure and the extended energy loss fine structure (EXELFS), which corresponds to the familiar EXAFS found in X-ray absorption spectra. Progress can also be expected in electron microscope design, leading to the availability of instruments on which both high resolution imaging and microanalysis can be performed simultaneously. At present, it is usually necessary to perform these functions on different instruments.

3 MAGIC ANGLE SPINNING NMR

3.1 Introduction

Once the composition of a new material has been established, a wide range of physical methods is available for further characterisation. Diffraction methods, of course, play a vital role, but spectroscopic and resonance techniques, including infrared, Raman, and UV-visible spectroscopies, and NMR, ESR, and Mossbauer measurements, can also provide valuable information. All of these methods are well established, but only recently has it become routinely possible to obtain high resolution NMR spectra from powders, by using the technique of magic angle spinning which was first proposed by Andrew and co-workers¹⁵.

NMR spectra of solids, in contrast to those of liquids, typically show broad absorptions in which the characteristic features of a solution spectrum—the chemical shift and spin-spin coupling information—are obscured. The purpose of the high resolution experiment is to remove these broadening effects whilst retaining the chemical information contained in the spectrum. Line broadening can arise from a range of anisotropic interactions¹⁶. Dipole-dipole interactions, between nuclei of the same element or between different spin types, are a common source of broadening, especially in hydrogen-containing materials. The effect is distance dependent ($1/r^3$) and can therefore be drastically reduced by dilution, for example, homonuclear dipolar broadening is not a problem with ^{13}C spectra. Heteronuclear interactions involving hydrogen are normally removed by broad band decoupling. A second important effect arises from the unsymmetrical nature of the chemical shift: the chemical shift anisotropy. In a single crystal experiment, the chemical shift of the resonance depends upon the orientation of the crystal, and thus the magnetic

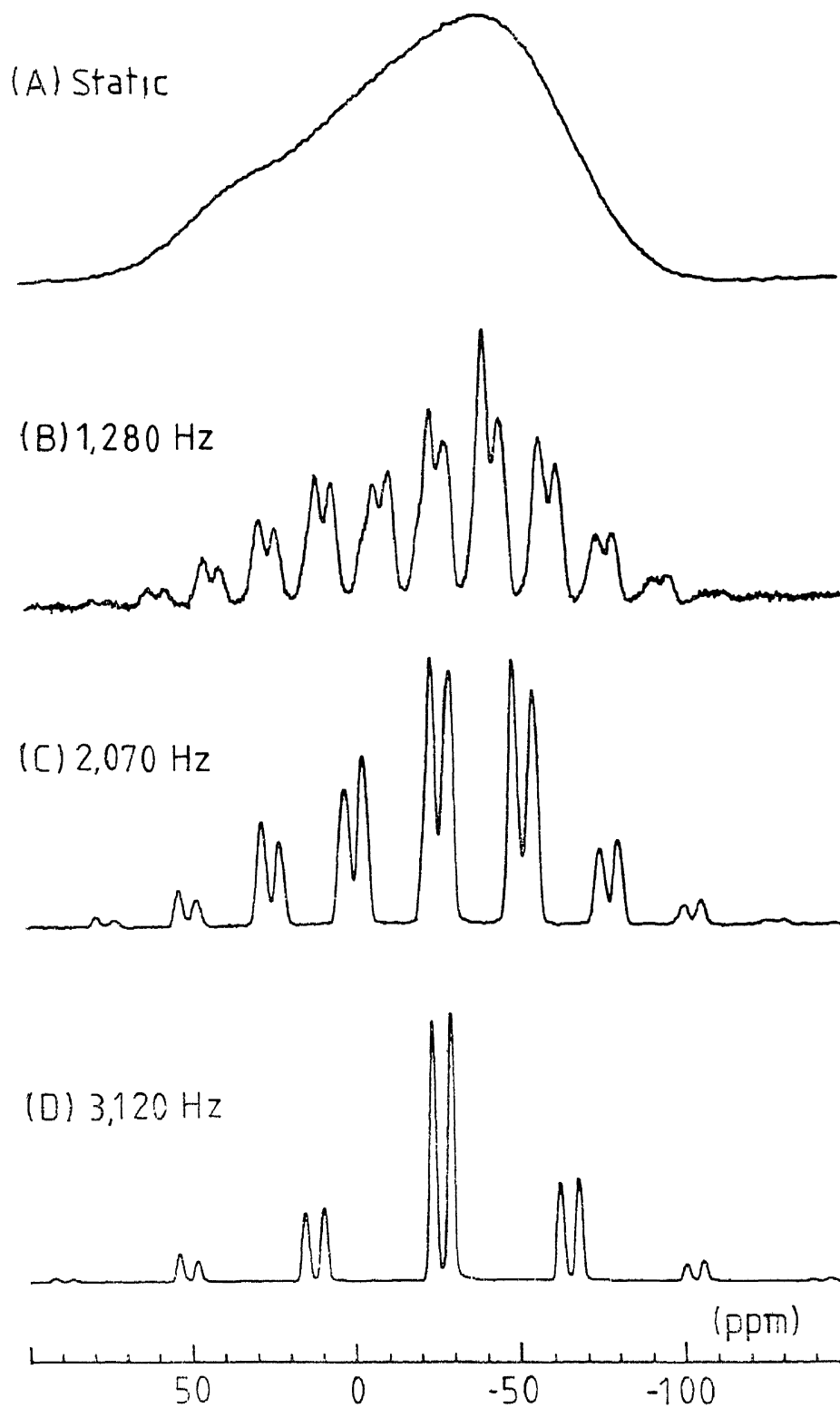


FIG 6 The ^{31}P NMR spectrum of KAlP_2O_7 as a function of spinning speed at the magic angle¹⁷

moments of the nuclei, with respect to the direction of the applied magnetic field. With a powder, however, a wide range of crystallite orientations is present and a

broad envelope of resonances is observed. This is an important contribution to the broadening in most solid state spectra. Third, the presence of quadrupolar nuclei ($I > 1/2$) will also contribute to the line width. Most of the work to date has been performed on spin $1/2$ nuclei, but quadrupolar nuclei with non-integral spins can also be studied by high resolution methods, because the $1/2 \rightarrow -1/2$ transition is unaffected by quadrupolar interactions, to a good approximation. Such measurements are best performed at high fields.¹⁶

A static ^{31}P spectrum of KAlP_2O_7 is shown in Fig 6(A).¹⁷ From such a spectrum, it is possible to extract the principal elements of the chemical shift tensor, σ_{11} , σ_{22} , σ_{33} , although this will be difficult if more than one type of phosphorus is present. The anisotropic spectrum may be averaged to the isotropic value by the technique of magic angle spinning (MAS), in which the sample is spun rapidly around an axis inclined at the so-called magic angle, $\theta = 55^\circ 44'$, with respect to the magnetic field. The spinning speed must be comparable with the frequency spread of the shift anisotropy. The effect of increasing the spinning rate on the ^{31}P spectrum of KAlP_2O_7 is shown in Fig 6. At 3120 Hz, two independent phosphorus atoms, with isotropic resonances $\sigma_{\text{iso}} = 1/3 (\sigma_{11} + \sigma_{22} + \sigma_{33})$ at -23.7 and -29.1 ppm (from 80 per cent H_3PO_4) are observed. These are flanked by "spinning side bands", which are separated by the spinning speed and arise because the spinning frequency is not quite sufficient to remove all the anisotropy. It is a straightforward matter to determine the principal elements of the shielding tensor from such a spectrum, even if more than one site is present.¹⁸

Finally, we note that the technique of cross-polarisation (CP) can be used to increase the sensitivity of the MASNMR method to dilute nuclei.¹⁹ The basic principle is that the magnetisation of the dilute nucleus is enhanced by coupling it to the magnetisation of an abundant nucleus, usually hydrogen. In the first application of this method by Schaefer and Stejskal,²⁰ the ^{13}C spectra of a series of natural polymers were greatly improved by the use of a combined CP-MAS technique. The resolution is unaffected by cross polarisation.

3.2 Applications

There are several ways in which MASNMR methods can contribute towards the characterisation of a polycrystalline material. If the structure is unknown, then the spectrum may reveal the number of crystallographically distinct atoms of the resonating nucleus. In the zeolite ZSM-5, for example, the ^{29}Si spectrum, reveals at least nine resonances, consistent with the space group Pnma .²¹ A recent study of $\alpha\text{-CaZn}_2(\text{PO}_4)_2$ provides another interesting illustration. The ^{31}P MASNMR spectrum (Fig 7) shows two resonances, with isotropic shifts at 2.2 and 10.0 ppm, and since the unit cell is triclinic, the structure must belong to the centrosymmetric space group $\text{P}\bar{1}$ rather than the non-centric P1 .²²

If the structure is known, the MASNMR method may provide a unique probe of any local ordering that may be present. Again, a great deal of work has been done on zeolites, where the ^{29}Si spectra are sensitive to the numbers of aluminiums

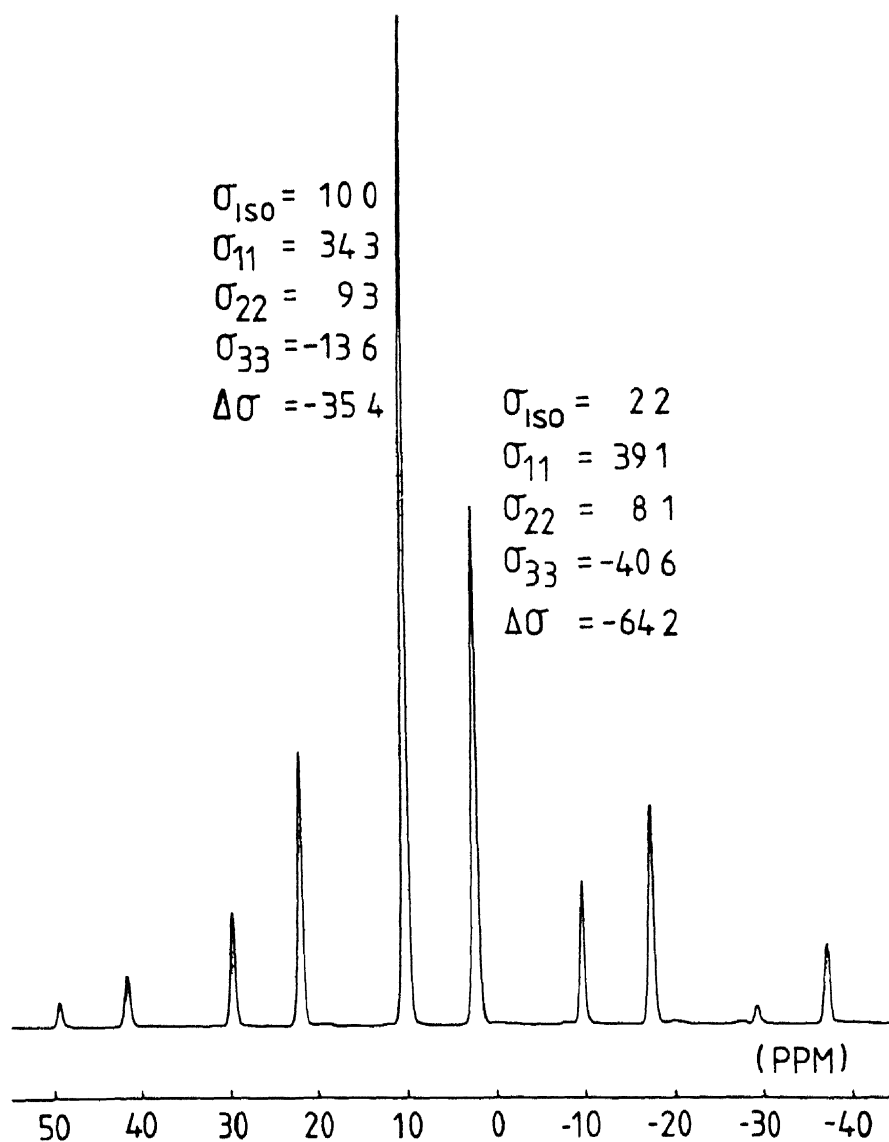


FIG 7 The ^{31}P MASNMR spectrum of $\alpha\text{-CaZn}_2(\text{PO}_4)_2$, showing two crystallographically distinct phosphorus sites, each with spinning sidebands ²²

in the next nearest neighbour sites ²³ This has lead, for example, to the proposal of several schemes for the ordering of silicon and aluminium in the aluminosilicate framework of zeolite-Y ²⁴ In a rather different example, it has been shown that the ^{31}P spectra of $\text{Zn}_{3-x}\text{Mg}_x(\text{PO}_4)_2$ solid solutions are extraordinarily sensitive to the distribution of zinc and magnesium over the two available cation sites in the structure, one of which is octahedral and the other five coordinated ²⁵ In other circumstances, a full refinement of the crystal structure would be needed to obtain this information

In order to take full advantage of MASNMR data, it is necessary to be able to assign the observed peaks to particular atoms in the crystal structure, but it has proved difficult to do this because of the wide range of factors that influence the chemical shift. However, several empirical attempts have been made to relate

isotropic chemical shifts to structural features. For example, ^{29}Si shifts in minerals have been correlated with T-O-T angles,²⁶ Si-Si non-bonding distances²⁷ and with oxygen bond strengths,²⁸ calculated by the method of Brown and Shannon.²⁹ The correlation between ^{31}P chemical shifts and the bond strengths at the surrounding oxygen atoms is shown in Fig 8.²² Such correlations provide a useful aid to peak assignment, but further progress will depend upon a more rigorous analysis of the problem and greater use of anisotropic shift data.

But the most important area of current development, which will have a major impact on solid state chemistry, is the application of MASNMR methods to a wider range of nuclei. The list is already long, and includes ^{19}F , ^{23}Na , ^{27}Al , ^{51}V , ^{113}Cd , and ^{195}Pt , but many other nuclei have yet to be explored in detail and rapid growth can be expected in this area.

4. POWDER DIFFRACTION METHODS

4.1 Introduction

X-ray powder diffraction methods play a central role in the study of polycrystalline materials. Data collection on a modern powder diffractometer is rapid and can yield precise d -spacing and intensity information. The applications of this technique are several, including

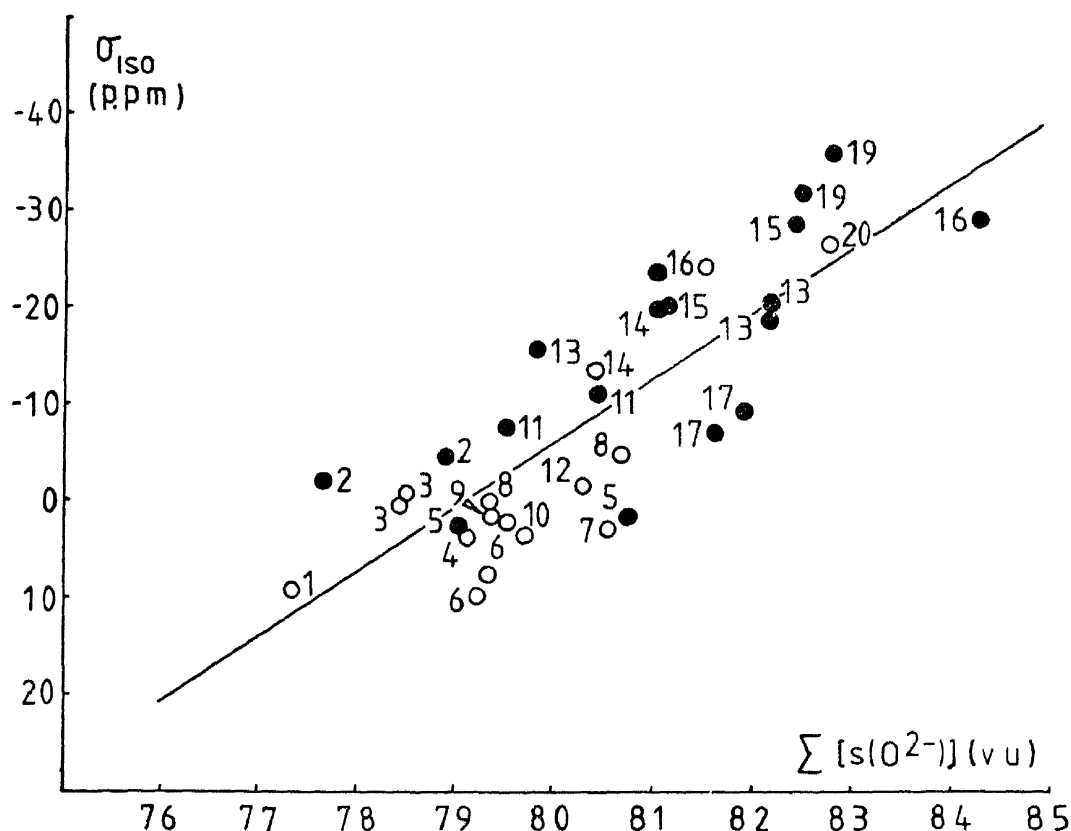


FIG 8 Plot of correlation between ^{31}P isotropic chemical shift data and bond strengths at oxygen, for a series of metal phosphates ²²

(1) Qualitative analysis, in which the d -spacing data of a material are compared with values found in a comprehensive database such as the Powder Diffraction File; this can also be used in the identification of mixtures, especially with the assistance of suitable "search and match" software.

(2) Quantitative analysis of mixtures, in which the relative intensities of selected reflections of the constituent phases are compared with those in standard mixtures.

(3) Phase equilibria studies, in which the powder pattern is monitored as a function of composition or temperature

The importance of this type of work is reflected in its widespread use, but it is essentially limited to the characterisation of known phases. New materials are, of course, routinely fingerprinted by powder X-ray diffraction, but here we examine the extent to which powder methods can yield more sophisticated information, including the crystal structure, itself. We shall consider the use of both X-rays and neutrons

The determination of the structure, whether by single crystal or powder methods, can best be understood in terms of a series of discrete steps:

- (1) indexing of the diffraction pattern and the determination of the crystal system (eg. cubic, orthorhombic, etc.) and lattice parameters,
- (2) identification of the space group;
- (3) solution of the phase problem and determination of the approximate structure, and
- (4) refinement of the structure

With single crystal X-ray data collected on an automatic diffractometer, this sequence of steps is normally routine. The unit cell can be identified from an automatic peak search, the space group determined from systematic absences, and the phase problem solved by Patterson or direct methods. The structure can then be refined by using a combination of least-squares and difference Fourier techniques. With powders, however, there are serious difficulties, most of which arise because of peak overlap which results when the three-dimensional intensity data is compressed into a single dimension in the powder experiment. Indexing of the reflections and unit cell determination are non-trivial, even with the aid of a good auto-indexing computer programme. These require very precise d -spacing data, and the use of an internal standard is recommended. Selected area electron diffraction is also of value in obtaining single crystal diffraction patterns from powder samples. Even if the cell can be found successfully, the subsequent steps may still be insurmountable. In particular, the solution of the phase problem is likely to be difficult, largely because the overlapping of adjacent reflections, which is especially marked with powder data of low symmetry systems, introduces ambiguity into the assignment of intensities to particular hkl values. This information is essential for both Patterson and direct methods calculations. For this reason *ab initio* structure

determination using powders has remained an empirical rather than an exact science. Some of the approaches that have been used are described in section 4.4. First, however, we shall examine the progress that has been made in the *refinement* of structures from powder data.

4.2 Rietveld Profile Analysis

The most striking advance in powder techniques during the last twenty years has been the advent of structure refinement by the method of Rietveld profile analysis.³⁰ This was initially developed for the analysis of neutron data, but, as we shall see, has also been applied to X-ray data. We have already noted that it may not be possible to determine an extensive set of integrated intensities, $I(hkl)$, from a powder profile, but Rietveld showed that it is nevertheless feasible to refine the structure by a careful fitting of the complete profile. The lattice parameters define the 2θ value of each reflection, and an approximate model for the structure is required in order to estimate the intensities of the reflections. By assuming that the reflections are Gaussian in shape, Rietveld showed that the whole profile could be calculated and the structure then refined by a curve-fitting least-squares procedure. This important breakthrough extended the scope of powder techniques, at a stroke, from simple cubic and hexagonal systems to low symmetry materials. As an example, a refinement of the structure of Ba_2ReO_5 , in space group $P2_1/m$, is shown in Fig 9.³¹

The facility with which the Rietveld method can be applied to constant wavelength neutron powder data stems largely from the simplicity of the peak shape, which is usually well described by a Gaussian function, but the method has been

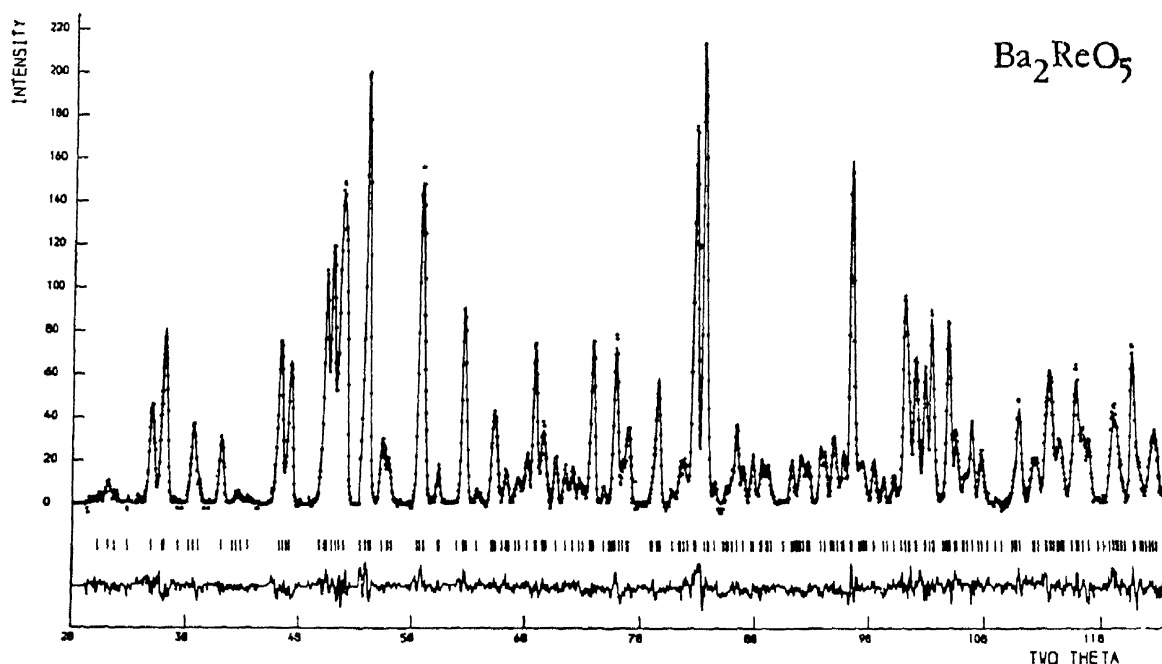


FIG 9 Observed (dots) and calculated (full line) powder neutron diffraction profiles of Ba_2ReO_5 .³¹ Reflection positions and a difference curve are also shown.

extended more recently to X-ray powder data³² and time-of-flight neutron diffraction data (*see below*). It remains, however, a method by which structures are refined, and does not, in itself, provide a means of obtaining the necessary starting model. This limitation is considered in sections 4.4 and 4.5.

4.3 Time-of-Flight Neutron Diffraction

A conventional powder experiment employs a fixed-wavelength incident beam and a counter which measures the scattered intensity by sweeping through a range of scattering angles, 2θ . In the time-of-flight (TOF) method, the neutron beam is white and pulsed (say, 50 pulses per second). The diffraction pattern is collected by measuring the time of arrival of neutrons with different wavelengths (and, therefore, velocities) at a fixed angle counter, or time-focused counter bank (Fig 10). This is feasible with thermal neutrons, which have velocities of approximately 10^5 cm sec⁻¹. In terms of the Bragg equation, $\lambda = 2d \sin \theta$, θ is fixed and λ is varied. A typical TOF pattern is shown in Fig 11. As in the constant wavelength technique, Rietveld profile analysis can be performed³³. Pulsed neutron sources for condensed matter research are available in Japan, the U.S.A., and Great Britain.

4.4 Structure Determination with Powder Data . Empirical Methods

The determination of structures from powder data, with or without profile analysis, has focused on obtaining starting models by one of three methods

- (1) identification of an apparently isostructural material of known structure,
- (2) use of difference Fourier methods to investigate derivatives of known structures, and
- (3) trial and error methods

Method (1) is widely used, normally by means of searching the data bases for a compound with similar stoichiometry and lattice parameters to the unknown. Structures that have been determined in this way range from systems where the analogy is obvious (e.g. $\text{Cr}_2(\text{MoO}_4)_3$ and $\text{Fe}_2(\text{MoO}_4)_3$)³⁴ to those for which a certain amount of detective work is necessary: the profile refinement of Ba_2ReO_6 which adopts the same structure as Cs_2DyCl_5 , falls into the latter category (Fig 9).

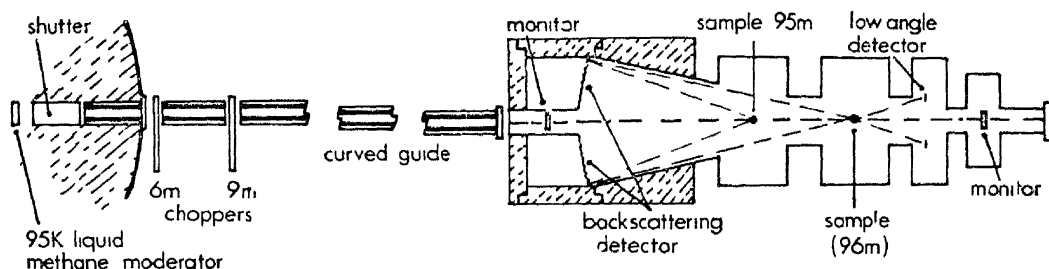


FIG 10 The high resolution powder diffractometer (HRPD) at the pulsed neutron source, ISIS, Rutherford-Appleton Laboratory, U.K. The source to sample distance is 96m. The backscattering detector bank covers the 2θ range 170° – 178° . Data from the different elements are time-focused in software.

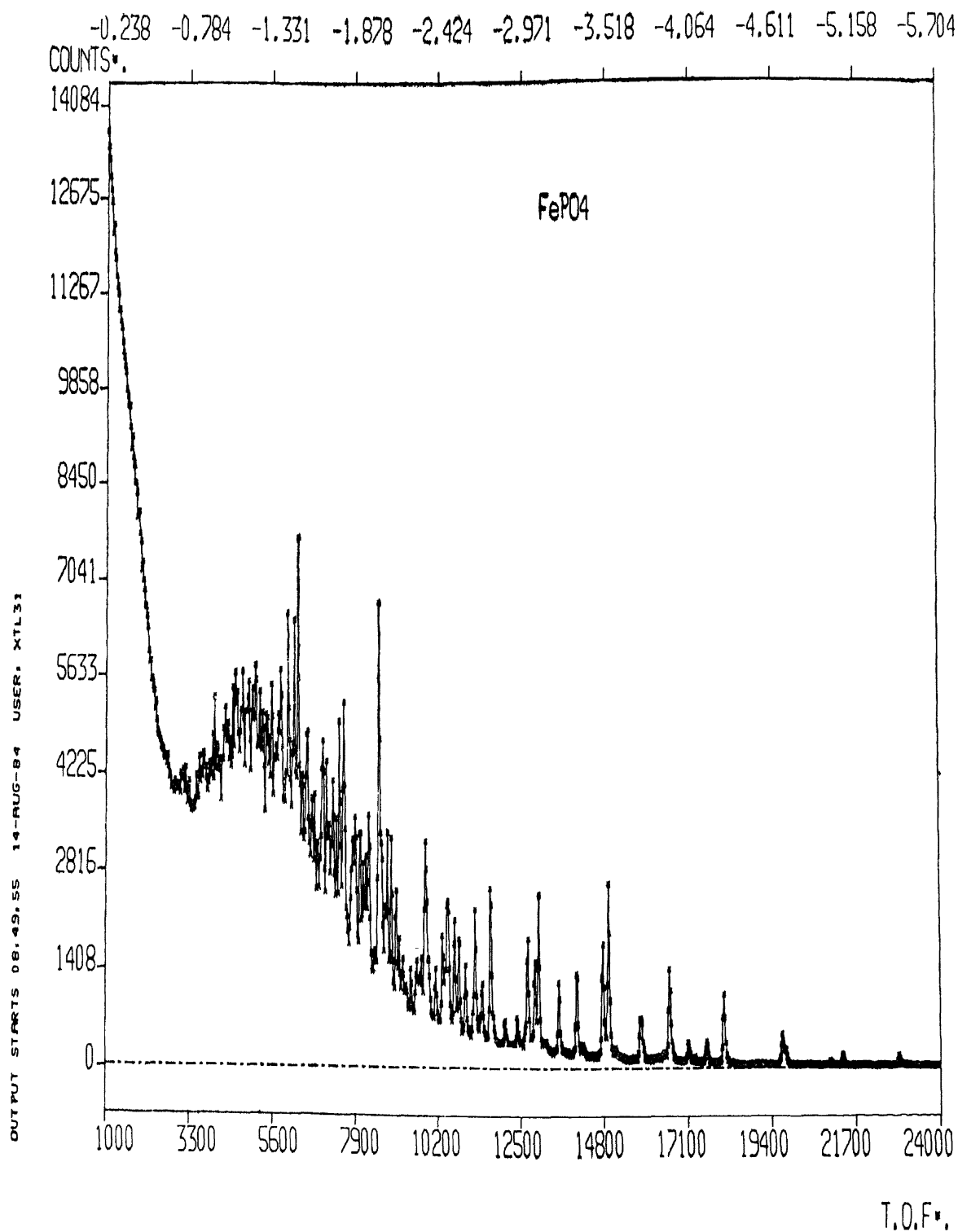


FIG 11 The TOF powder neutron diffraction pattern of FePO_4 , collected on GPPD at the Intense Pulsed Neutron Source, Argonne National Laboratory (Battie, Harrison and Cheetham, *unpublished*) The broad feature at short times-of-flight is due to epithermal neutrons

Method (2) has also been extensively exploited, but it suffers from the usual problem with powders there is a dearth of discreet integrated intensity information. However, when most of the atom positions have been located and refined, the Rietveld procedure provides a list of approximate observed $I(hkl)$'s which can be used with the calculated $I(hkl)$'s in a difference Fourier calculation. This approach should be used with caution, but it has been applied successfully to some interesting problems such as the location of adsorbed molecules in zeolite cages³⁵ and the positions of protons in complex oxides³⁶. This strategy is enormously valuable in solid state chemistry, but, like method (1), it is obviously unsuitable for the characterisation of entirely new structure types.

For entirely new structures, workers have been forced to rely on trial and error approaches. This has usually involved the use of both X-ray and neutron data, the former being used to determine heavy atom positions from radial distribution functions. The work of Taylor on uranium tetrabromide provides a good example, uranium was located with X-rays and the lighter halogen atoms were positioned by trial and error using neutron data³⁷. In another instance, the same methodology was used to solve the non-centrosymmetric superstructure of Bi_3ReO_8 ³⁸. This approach to structure solving, whilst sometimes unavoidable, is extremely time consuming and frequently unrewarding. In the following section, we shall describe some of the very latest developments that promise to take powder methods into a new and exciting phase in which trial-and-error procedures will become redundant.

4.5 *Ab Initio Structure Determination with Powder Data*

We have already noted that the main loss of information in a powder experiment arises from the overlapping of adjacent Bragg reflections which leads to ambiguities in their intensities. This information is essential if the classical methods of structure solving, used routinely in single crystal work, are to be employed. The new generation of powder diffractometers, at both neutron facilities and synchrotron sources, have such high resolution that this limitation should be largely overcome. The improvement in resolution leads to a dramatic reduction in the incidence of peak overlap. Indeed, the instrumental resolution is now so good (e.g. $\Delta d/d = 0.04$ per cent on the high resolution powder diffractometer (HRPD) at the Rutherford Laboratory, U.K.), that most samples show line broadening due to particle size and strain effects.

This promise has yet to be fulfilled, but the feasibility of solving known structures from powder data by using direct methods has been demonstrated,³⁹ and one of the first experiments on HRPD illustrates what might be done with unknown structures. The material studied was FeAsO_4 , which was first reported by Shafer *et al.*⁴⁰ Subsequently, D'Yvoire indexed the X-ray powder pattern according to a monoclinic cell, assigned the space group $P2(1)/n$, and on the basis of infrared evidence and the facile transformation of the monoclinic modification to one with the CuSO_4 structure, suggested that the iron atom might be octahedrally coordinated.⁴¹ Data for FeAsO_4 , collected on HRPD at the Spallation Neutron Source

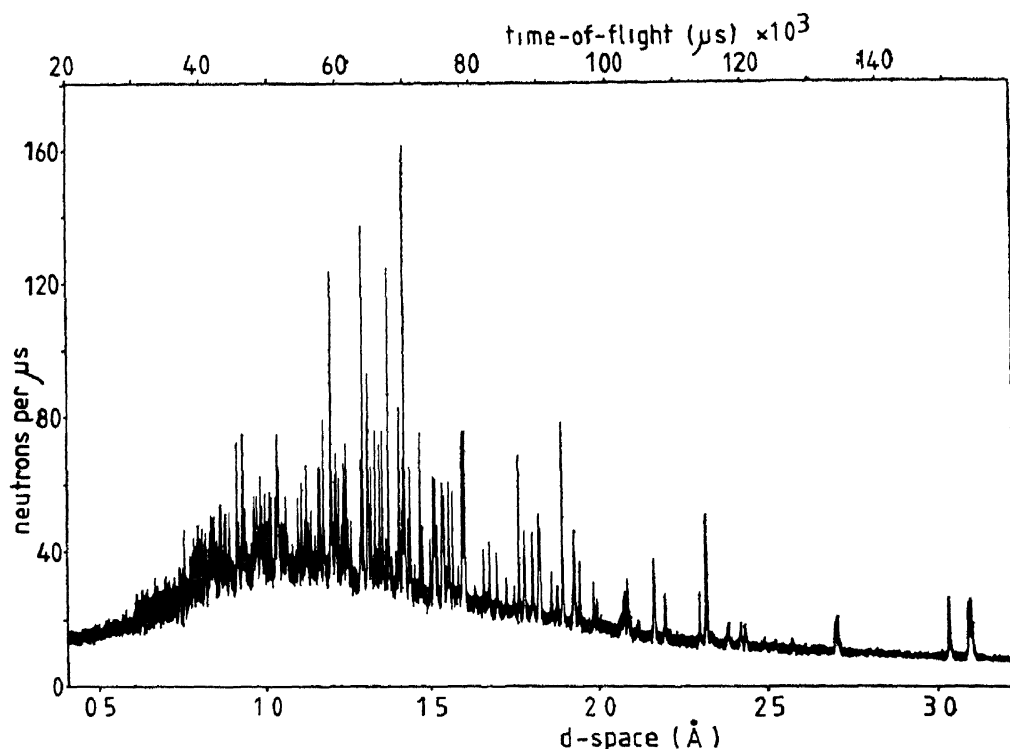


FIG 12 The TOF powder neutron diffraction pattern of FeAsO_4 , collected on HRPD at ISIS.⁵ Note the extraordinary resolution. The epithermal neutrons, which are seen in the pattern of FePO_4 (Fig 11) are removed by the neutron guide.

(ISIS) are shown in Fig 12.⁵ The correctness of the cell proposed by D'Yvoire was first confirmed by auto-indexing of the pattern using the programme FZON,⁴² and the lattice parameters were then refined and the space group confirmed by examining the systematic absences. Integrated intensities, $I(hkl)$, were then obtained manually for 139 reflections, including approximately 60 weak reflections. It is this stage that is facilitated by high resolution, since peak overlap, which normally leads to ambiguities in the intensities of individual Bragg reflections, is minimised. Structure factor amplitudes were then calculated according to the relationship:

$$I(hkl) = \lambda^4 m F(hkl)^2,$$

where m is the multiplicity of reflection hkl and λ is the wavelength at which it is measured. The $F(hkl)$ values were then used as the input for direct methods analysis using the programme MITHRIL.⁴³ Neutron data are normally well suited to direct methods analysis because neutron scattering lengths fall within a narrow range of values. In the FeAsO_4 analysis, both triplets and negative quarters were calculated. The peak list from the calculation with the highest figure of merit is shown in Table I. Analysis of the interpeak distances and angles confirmed that a chemically sensible solution had been found, with peaks 1 and 2 corresponding to Fe and As, respectively, and peaks 3–6 to oxygen. Note that the peaks appear in order of their neutron scattering lengths and that there is a substantial gap between peaks 6 and 7, the latter indicates the level of noise in the map. The coordi-

nates obtained from the direct methods analysis were then refined to yield the structure shown in Fig 13. One of the interesting features of the structure of FeAsO_4 which, surprisingly, is isostructural with LiAlH_4 , is the presence of five coordinated iron sites which share a common edge

TABLE I
Direct methods solution for FeAsO_4

Peak No	<i>x</i>	<i>y</i>	<i>z</i>	height
1	0.322	0.051	0.242	2691
2	0.925	0.179	0.257	1960
3	0.369	0.244	0.087	1320
4	0.485	0.127	0.631	1199
5	0.102	0.046	0.322	1193
6	0.790	0.080	0.087	1104
7	0.062	0.087	0.726	591
8	0.885	0.117	0.887	590

No. of reflections = 139

Triplets generated from top 66 reflections

Negative quartets generated from top 67 reflections

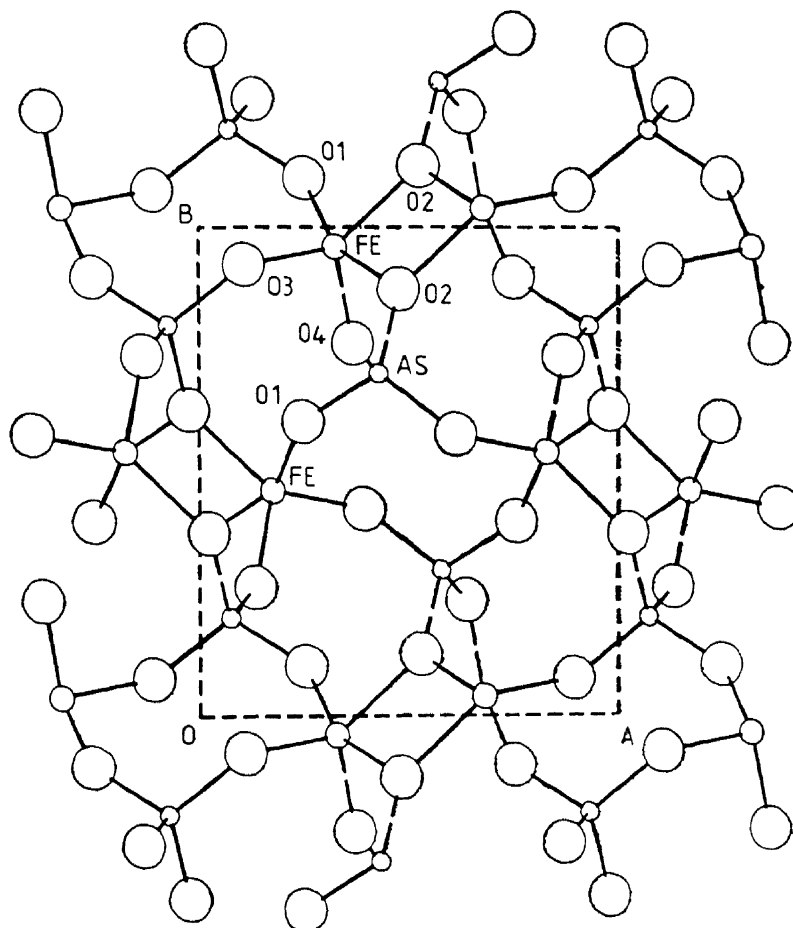


Fig 13 The crystal structure of FeAsO_4 , viewed down $[001]$

Recent developments in high resolution X-ray instrumentation suggest that similar progress can be expected in this area, and at the time of writing, the crystal structure of α -CrPO₄ has just been determined from synchrotron powder data obtained at the National Light Source, Brookhaven.⁴⁴ The orthorhombic structure, with 8 atoms in the asymmetric unit, was solved by Patterson methods by using a vector search procedure.

The success of these very recent works augurs well for future structure determination with powders. Direct methods will no doubt, be preferred with neutron data, but the use of Patterson techniques should not be neglected as a means of locating strong scatterers. High resolution X-ray data should be amenable to both approaches. Single crystal methods will continue to be the preferred medium for structure determination, but powder techniques now offer a viable alternative.

4.6 Applications

The applications of powder methods to structure determination, mainly using the empirical methods described in section 4.4, are varied and increasingly numerous, and the use of the Rietveld method has grown from a handful of paper per annum in the early 70's to 150 in 1984. Applications to solid state chemistry were reviewed by Cheetham and Taylor in 1977⁴⁵ and more recently by Hewat,⁴⁶ who referenced approximately 250 studies on oxides, hydrides, halides, alloys, and minerals. The bulk of the work has involved neutron diffraction, for which the treatment of the peak shape is more straightforward, but X-ray Rietveld analysis is increasingly popular, especially with the availability of more sophisticated computer programmes. For example, Baerlocher⁴⁷ has developed a programme that incorporates slack constraints, of the type described by Hendrickson and Konnert,⁴⁸ into the least-squares refinement. This has been used to refine complex zeolite structures such as that of ZSM-5.⁴⁹

One measure of the scope of structure determination with powder data is the complexity of the problems that can now be tackled. The current state of the art is that structural models with about 100 parameters can be refined,³¹⁻⁵⁰ but the new generation of ultra-high resolution diffractometers is expected to increase this limit to 3-400. A recent study of potassium zeolite-L, containing pyridine, illustrates the sophistication of the problems that are now within reach.⁵¹ The position and orientation of the organic molecule inside the zeolite channel was determined at 4K (Fig. 14) and the results confirmed by means of molecular mechanics calculations, the experimental and calculated positions of the molecule agreed within 0.2 Å.

The future prospects for powder diffraction are extremely exciting. The use of high resolution methods for the *determination* of structure has already been described (section 4.5), but equally, promising is the utilization of high intensity sources for time-resolved experiments. With existing facilities, medium resolution neutron or X-ray diffraction patterns can be collected in a matter of minutes, but new sources will enable experiments to be performed in seconds, making possible the study of solid state reactions and other processes in real time.

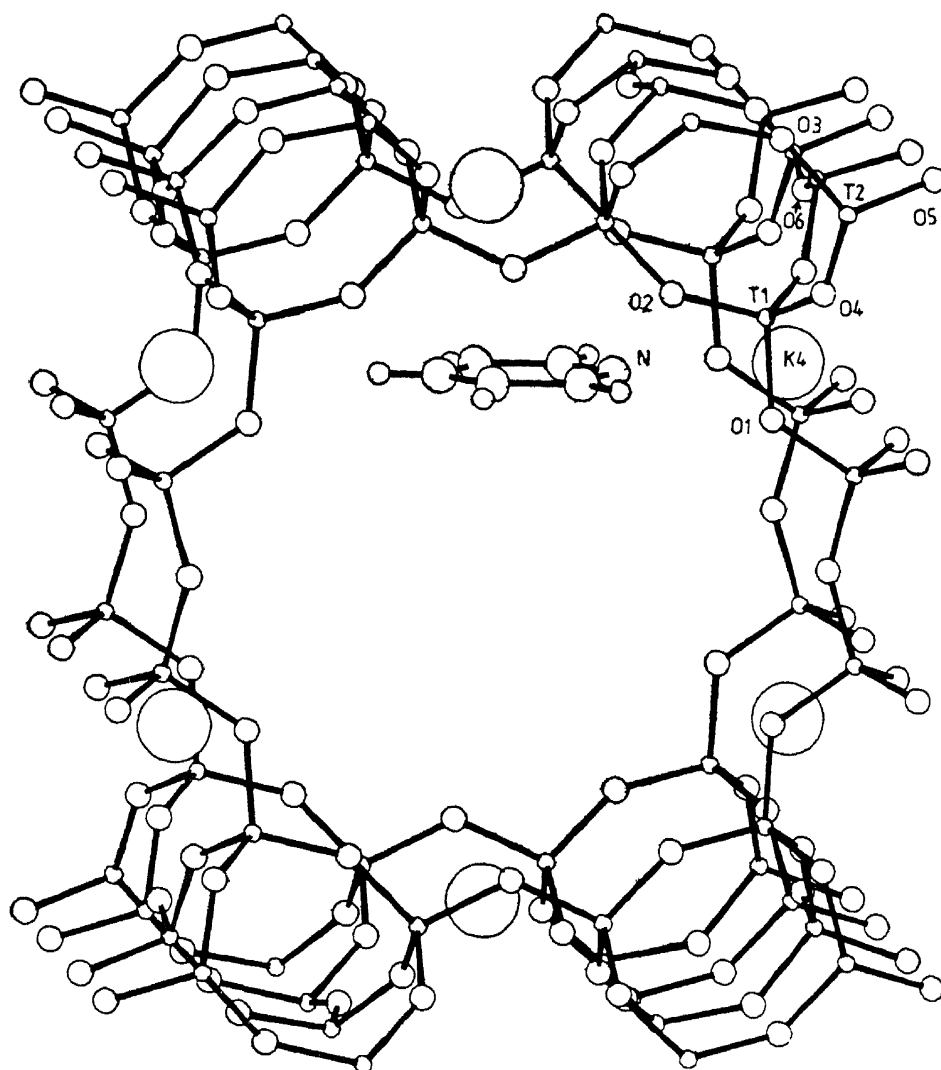


FIG 14 The location of pyridine in the main channel of potassium zeolite-L⁵¹ Note that the molecule lies close to the wall of the channel, optimising short range interactions, whilst enjoying an acid-base interaction with the potassium, K(4)

5 CONCLUSIONS

This brief review of some of the methods that are now being used to study powders has inevitably been selective. Many important techniques, such as Mossbauer spectroscopy and EXAFS, have been omitted, but attention has focused on those methods that have widespread applicability and where the recent developments have been most striking. One important omission is high resolution electron microscopy (HRTEM). The availability of high energy (3-400 KeV) transmission instruments with improved objective lenses has brought the resolving power of the electron microscope down to the atomic level, thus offering an alternative means of structural characterisation for powders. It should be noted that an HRTEM image represents a projection of the structure down the axis of viewing, and is therefore ideal for studying new structure with a short crystallographic axis. This has been demonstrated as a means of characterising new phases,⁵² especially when it is com-

bined with image simulations,⁵³ but it is best applied to the study of materials of known architectural type, such as the niobium oxide block phases. For entirely new structure types, modelling by trial-and-error methods is necessary. In addition, it should be noted that HRTEM does not yield atomic coordinates, and therefore bond lengths and bond angles, with the precision that is obtainable with X-ray and neutron diffraction. Nevertheless, in some areas, it is pre-eminent, especially in the study of structural defects.

We have noted not only the strengths of the techniques that have been described, but also their limitations, thus underlining the weakness of a single pronged attack on the characterisation of materials. The complementarity of the methods that are now available, however, is self-evident, and the most efficacious approach to a problem is likely to be one that harnesses the advantages of several techniques. When subjected to a multifaceted attack of this type even the most stubborn of problems is likely to yield.

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LOW-TEMPERATURE SYNTHESIS OF NOVEL METAL OXIDES BY TOPOCHEMICAL REACTIONS*

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Synthesis of a variety of novel metal oxides has been achieved at low temperatures by topochemical reactions. Thus topochemical dehydration of $\text{Mo}_{1-x}\text{W}_x\text{O}_3 \cdot \text{H}_2\text{O}$ provides a convenient route for the synthesis of $\text{Mo}_{1-x}\text{W}_x\text{O}_3$ in ReO_3 -type structure. Dehydration of $\text{HMoO}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ to HMoO_2PO_4 results in a topotactic transformation of the parent chain structure to a layered structure in the product. Exchange of lithium with protons in LiNbWO_6 and LiTaWO_6 results in a novel structural transformation from the rutile to the ReO_3 structure of the product phases, HNbWO_6 and HTaWO_6 . Topotactic reduction of LaNiO_3 and LaCoO_3 yields new vacancy-ordered perovskite-related phases, $\text{La}_2\text{Ni}_2\text{O}_5$ and $\text{La}_2\text{Co}_2\text{O}_5$, that cannot be synthesized otherwise. Hydrogen can be inserted topotactically into LaNiO_3 and LaCoO_3 around ambient temperatures in the presence of Pt-catalyst to yield H_xLaNiO_3 and H_xLaCoO_3 . Insertion of bismuth into WO_3 yielding *intergrowth tungsten bronzes*, Bi_xWO_3 , can also be viewed as a topotactic process. The investigations reveal that it is possible to design imaginative routes for the synthesis of metal oxides at low temperatures making use of topochemical reactions.

Key Words : Synthesis of Metal Oxides; Topochemical Reactions; Dehydration; Ion-Exchange; Reduction; Insertion/Extraction.

INTRODUCTION

SYNTHESIS and structural characterization of solids constitute an important activity of solid state chemists¹. Conventionally, solid state synthesis is carried out by the ceramic method which involves mixing the reactants and heating them at high temperatures. The limitations of this crude approach are too well known to be recounted here.² In recent years, efforts have been made to design imaginative routes for solid state synthesis based on novel chemical reactions.³ A number of common chemical reactions involving inorganic solids such as dehydration, decomposition, oxidation, and reduction are known to proceed *topochemically* to yield well-defined products that bear definite structural relationships with the starting materials.^{4,5} Reversible insertion and extraction of atomic and molecular species into layered solids *via* redox and ion-exchange processes is another topochemical reaction that is being increasingly investigated.^{6,7} Topochemical relationship has recently been shown to exist between NiO and Ni when the oxide is reduced to the metal.⁸ Such topochemical reactions which occur at relatively mild conditions provide 'soft' (low-temperature) routes for solid state synthesis.

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Synthesis of solids at low temperatures has several attractive features. Homogeneous and pure products with large surface areas can be obtained with relative ease. Metastable phases that cannot be prepared by high temperature methods can be stabilized by low temperature methods. More importantly, in view of the structural relationships existing between the parent and product solids in topochemical reactions, it is possible to engineer the synthesis *via* topochemical reactions, to yield solids possessing the desired structures.

We have made use of topochemical dehydration, ion-exchange, oxidative deintercalation, reduction and insertion of atomic species (H, Bi) into oxide hosts to synthesize a variety of novel metal oxides. Thus topochemical dehydration of $\text{Mo}_{1-x}\text{W}_x\text{O}_3 \cdot \text{H}_2\text{O}$ and $\text{HMoO}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ has enabled the synthesis of ReO_3 -like $\text{Mo}_{1-x}\text{W}_x\text{O}_3$ and layered HMoO_2PO_4 . Exchange of lithium with protons in LiNbWO_6 and LiTaWO_6 has resulted in the formation of ReO_3 -like HNbWO_6 and HTaWO_6 , the ion-exchange being accompanied by a topotactic structural transformation from rutile to ReO_3 structure. Oxidative deintercalation of lithium from LiVO_2 an Li_2MoO_3 possessing ordered rocksalt structure has yielded new $\text{Li}_{1-x}\text{VO}_2$ and $\text{Li}_{2-y}\text{MoO}_3$ members where the cubic close packed anion array is preserved. An interesting example of solid state synthesis of metastable phases is that of $\text{La}_2\text{B}_2\text{O}_5$ ($\text{B} = \text{Co}, \text{Ni}$) from LaBO_3 perovskites *via* topochemical reduction. Significantly, when the same parent oxides are treated with hydrogen in the presence of platinum at room temperature, hydrogen-insertion products, H_xLaBO_3 , are obtained instead of anion deficient phases. Similar hydrogen insertion has also been carried out with HNbWO_6 , HTaWO_6 and $\text{Mo}_{1-x}\text{W}_x\text{O}_3$ to yield hydrogen bronzes. Another interesting example of topochemical insertion is that of Bi into WO_3 yielding *inter-growth tungsten bronzes* (ITBs) wherein WO_3 slabs of finite width intergrow coherently with strips of HTB structure. The results of these investigations presented in this paper reveal that it is possible to design imaginative methods for the synthesis of a variety of metal oxides based on topochemical reactions.

EXPERIMENTAL

$\text{Mo}_{1-x}\text{W}_x\text{O}_3 \cdot \text{H}_2\text{O}$ ($0 < x \leq 1$) solid solutions were prepared by adding a solution of MoO_3 and WO_3 in aqueous ammonia to hot (60°C) 6M HNO_3 under constant stirring.⁹ $\text{HMoO}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ was prepared by adding a viscous solution of MoO_3 (10g) in concentrated H_3PO_4 (30ml) to 250ml of concentrated nitric acid.¹⁰ On evaporation, white crystals of $\text{HMoO}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ separated out. LiNbWO_6 and LiTaWO_6 of trirutile structures were prepared by reacting the required quantities of Li_2CO_3 , WO_3 , $\text{Nb}_2\text{O}_5/\text{Ta}_2\text{O}_5$ at 800°C for 24h. LiVO_2 was prepared by reacting Li_2CO_3 and V_2O_5 in hydrogen atmosphere, first at 500°C for 4h and then at 700°C for 10h. Li_2MoO_3 was prepared by hydrogen-reduction of Li_2MoO_4 at 650°C .^{10a} LaCoO_3 and LaNiO_3 were prepared by methods reported in the literature.¹¹ Bi_xWO_3 ($x \leq 0.1$) were prepared by heating Bi metal with WO_3 in sealed evacuated silica tubes at 900°C .^{11a}

Dehydration and reduction reactions involving a weight loss were followed thermogravimetrically using a Sartorius Microbalance at heating rates of $2\text{--}5^\circ$

per minute Proton-exchange of lithium in LiNbWO_6 and LiTaWO_6 was carried out by refluxing the solids in hot aqueous H_2SO_4 (9–13M) Delithiation of LiVO_2 and Li_2MoO_3 was carried out by treating the oxides with Br_2 in CHCl_3 at room temperature Hydrogen insertion into LaNiO_3 , LaCoO_3 and $\text{Mo}_{1-x}\text{W}_x\text{O}_3$ was carried out at 30–100 °C by passing hydrogen over the oxides dispersed with 0.5 per cent Pt by weight.

The solids were characterized by X-ray diffraction, electron diffraction and i.r. absorption spectroscopy. X-ray powder diffraction patterns were recorded with a JEOL JDX-8P diffractometer or a Philips diffractometer (PW 1050/70) using CoK_α or CuK_α radiation. Electron diffraction patterns were recorded with a JEOL 200CX electron microscope.

RESULTS AND DISCUSSION

Topochemical Dehydration

Dehydration of several inorganic solids is known to proceed topochemically, typical examples being the transformation of brucite $[\text{Mg}(\text{OH})_2]$ to periclase $(\text{MgO})^{12}$ and $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ to anhydrous MoO_3 .¹³ We have investigated the topochemical dehydration of $\text{Mo}_{1-x}\text{W}_x\text{O}_3 \cdot \text{H}_2\text{O}$ and $\text{HMoO}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, which has enabled the preparation of $\text{Mo}_{1-x}\text{W}_x\text{O}_3$ and HMoO_2PO_4 , possessing novel structures

MoO_3 crystallizes in a layered structure (Fig. 1) involving corner- and edge-shared MoO_6 octahedra, while the analogous WO_3 adopts a ReO_3 -like structure where the WO_6 octahedra share all corners. Although both the structures are related,¹⁴ it has not been possible to transform MoO_3 to the WO_3 structure (or *vice-versa*). Nevertheless, it is known that MoO_3 can be stabilized in the WO_3 structure by partially substituting molybdenum by tungsten.¹⁵ Unfortunately, the preparation of $\text{Mo}_{1-x}\text{W}_x\text{O}_3$ by the ceramic technique is difficult due to the difference in volatilities of the parent oxides. The solid solution between the hydrated oxides, $\text{Mo}_{1-x}\text{W}_x\text{O}_3 \cdot \text{H}_2\text{O}$, could however be readily prepared by a wet method, since $\text{MoO}_3 \cdot \text{H}_2\text{O}$ and $\text{WO}_3 \cdot \text{H}_2\text{O}$ are isostructural.¹⁶ $\text{Mo}_{1-x}\text{W}_x\text{O}_3 \cdot \text{H}_2\text{O}$ adopt the same layered structure as $\text{MoO}_3 \cdot \text{H}_2\text{O}$ and $\text{WO}_3 \cdot \text{H}_2\text{O}$ with a monoclinic unit cell ($a \sim 7.5$, $b \sim 10.7$, $c \sim 7.3 \text{ \AA}$, $\beta \sim 91^\circ$). The hydrate solid solutions undergo dehydration around 230 °C to yield $\text{Mo}_{1-x}\text{W}_x\text{O}_3$ which crystallize in the monoclinic WO_3 structure ($a \sim 7.3$, $b \sim 7.4$, $c \sim 3.9 \text{ \AA}$, $\beta \sim 91^\circ$). The topotactic transformation of the hydrates to anhydrous solid solutions involves a collapse of the layers along the b -direction, the structure remaining essentially the same in the ac -plane (Fig. 1). The crystallographic orientational relationships between the parent and product oxides as established by electron diffraction are $(010)_{\text{hydr}} \parallel (010)_{\text{oxide}}$, $[100]_{\text{hydr}} \parallel [001]_{\text{oxide}}$ and $[001]_{\text{hydr}} \parallel [100]_{\text{oxide}}$. Interestingly, even the yellow $\text{MoO}_3 \cdot \text{H}_2\text{O}$ undergoes dehydration to yield a metastable ReO_3 -like MoO_3 which subsequently transforms to the layered variety.⁹

Oxides possessing corner-connected network of octahedra and of tetrahedra are of considerable current interest,^{17,18} typical examples being the vanadyl and

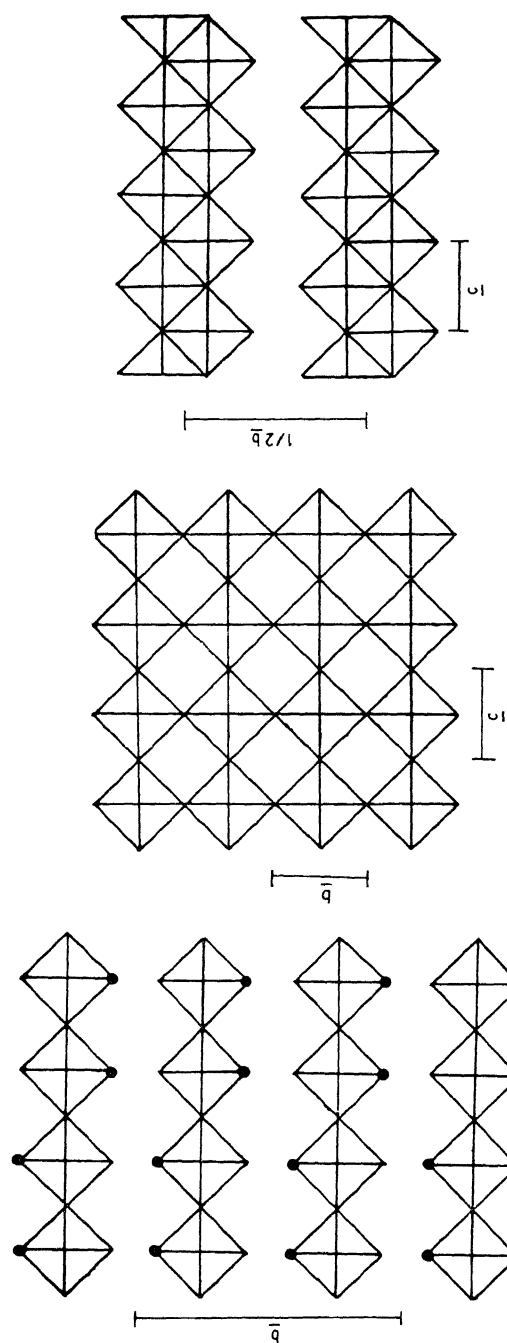


FIG 1 Schematic representation of the structures of MoO_3 (left), ReO_3 -like $\text{Mo}_{1-x}\text{W}_x\text{O}_3$ (middle) and layered MoO_3 (right).

molybdenyl phosphates. $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ is the prototype of this family of solids adopting a layered structure.¹⁹ Each VO_6 octahedron shares its equatorial oxygens with phosphorus; the two remaining axial oxygens consist of a vanadyl ($\text{V}=\text{O}$) oxygen and a water molecule coordinated *trans* to it. The structure is tetragonal ($a=6.215$, $c=7.40\text{\AA}$). $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ readily loses water topotactically to yield anhydrous VOPO_4 wherein the structural features of the parent are essentially preserved.

$\text{HMoO}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ is an interesting molybdenyl phosphate which adopts a chain structure (monoclinic, $a=6.73$, $b=6.32$, $c=7.03\text{\AA}$, $\beta=110.2^\circ$) consisting of alternating MoO_6 and PO_4 polyhedra, each MoO_6 and PO_4 share three vertices forming double chains (Fig. 2) which run parallel to the b -direction.²⁰ The chains

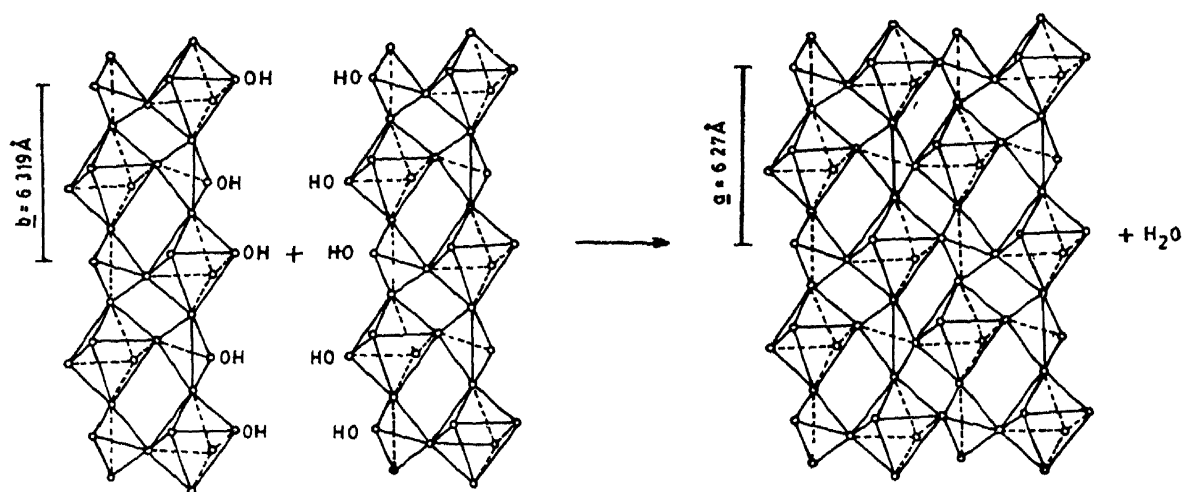


FIG 2 Schematic representation of the topotactic dehydration of $\text{HMoO}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ (left) to layered HMoO_2PO_4 (right)

are held together by hydrogen bonding. The position of hydrogen atoms are not known in this structure, but it is likely that they are attached to the unshared oxygen atoms of MoO_6 and PO_4 . Accordingly, the compound may be formulated as $\text{Mo}(\text{OH})_3\text{PO}_4$ or $\text{MoO}(\text{OH})_2\text{HPO}_4$. Since the building unit of this structure viz., alternating tetrahedra and octahedra, is essentially the same as that in $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$, we visualized that it may be possible to transform $\text{HMoO}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ to a layered structure similar to $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$, by topotactic elimination of water. We found that $\text{HMoO}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ readily loses one water molecule around 250°C yielding a new phase. X-ray diffraction pattern of the dehydration product (Table I) is different from that of starting material and could be indexed on a tetragonal cell with $a=6.27$ and $c=4.91\text{\AA}$. The new phase which could be written as $\text{MoO}(\text{OH})\text{PO}_4$ or $\text{MoO}_2(\text{HPO})_4$ is likely to possess a layered structure similar to $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$, having been formed by linking up the double chains laterally through elimination of water (Fig. 2). During the topochemical transformation, the structure essentially remains the same in the b -direction ($b=6.32\text{\AA}$ in the parent becomes $a=b=6.27\text{\AA}$ in the product).

TABLE I

X-ray powder diffraction pattern of HMoO_2PO_4 prepared by topochemical dehydration of $\text{HMoO}_2\text{PO}_4 \cdot \text{H}_2\text{O}$

<i>hkl</i>	$d_{\text{obs}}(\text{\AA})$ (I)	$d_{\text{calc}}^{(a)}(\text{\AA})$
001	4.91 (60)	4.91
110	4.49 (30)	4.43
101	3.92 (40)	3.87
111	3.31 (10)	3.29
200	3.13 (100)	3.13
002	2.42 (5)	2.45
220	2.21 (5)	2.22
112	2.16 (8)	2.15
221	2.01 (5)	2.02
310	1.97 (5)	1.98
311	1.81 (5)	1.84
320	1.76 (3)	1.74

$^{(a)}a = 6.27, c = 4.91 \text{\AA}$

Topochemical Ion-Exchange

Many complex metal oxides containing alkali metals undergo ion-exchange in aqueous or molten salt media retaining their structural features²¹. An interesting example of an ion-exchange reaction which is accompanied by a topotactic structural transformation is that of proton-exchange of LiNbO_3 and LiTaO_3 .²² The exchange results in the formation of cubic HNbO_3 and HTaO_3 possessing a ReO_3 -type structure. We have investigated the proton-exchange of lithium in LiNbWO_6 and LiTaWO_6 in aqueous acid solutions.²³ The exchange results in the formation of HNbWO_6 and HTaWO_6 which adopt cubic ReO_3 -like structure.

The primary products of proton-exchange of LiNbWO_6 and LiTaWO_6 are $\text{HNbWO}_6 \cdot \text{H}_2\text{O}$ and $\text{HTaWO}_6 \cdot \text{H}_2\text{O}$ as revealed by chemical analysis of tungsten and thermogravimetric analysis of water content. Both the phases are isomorphous adopting a simple cubic structure of ReO_3 type. The unit cell parameters derived from X-ray powder diffraction patterns (Fig. 3) are $a = 3.783(1) \text{\AA}$ for the niobium compound and $a = 3.807(2) \text{\AA}$ for the tantalum compound. The hydrated phases lose water to give anhydrous HMWO_6 ($\text{M} = \text{Nb}$ or Ta) around 400°C and $\text{MWO}_{5.5}$ around 600°C . Both HMWO_6 and $\text{MWO}_{5.5}$ also possess cubic ReO_3 -type structures (Fig. 3). It is indeed curious that $\text{MWO}_{5.5}$ adopts the ReO_3 structure since the composition is anion-deficient. On annealing the cubic $\text{NbWO}_{5.5}$ at 900°C for 12 hours, the phase transforms to a tetragonal structure (Fig. 3) with $a = 24.3$ and $c = 3.92 \text{\AA}$. The tetragonal phase appears to be related to tetragonal tungsten bronzes possessing a pentagonal column structure.²⁴

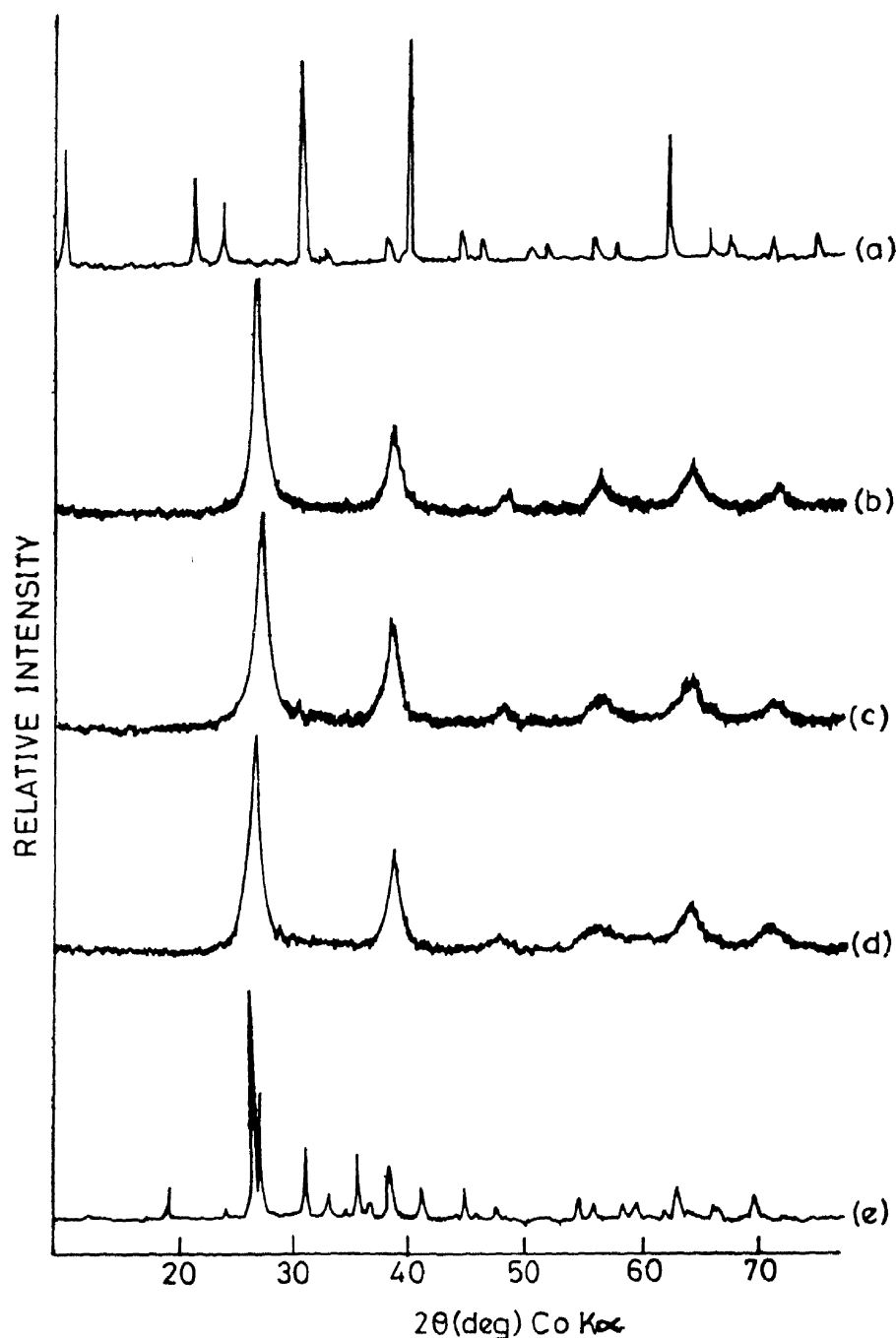


FIG 3 X-ray powder diffraction patterns of (a) LiNbWO_6 (trirutile), (b) $\text{HNbWO}_6 \cdot \text{H}_2\text{O}$, (c) HNbWO_6 , (d) NbWO_6 and (e) NbWO_6 after heating at 900°C for 12 hrs. Patterns (b)-(d) are cubic ReO_3 -like and pattern (e) is TTB-like.

Ion-exchange of LiMWO_6 to give HMWO_6 is accompanied by a transformation from the trirutile to the ReO_3 structure. A plausible mechanism for the rutile- ReO_3 transformation is shown in Fig 4. On ion-exchange, the tetragonal close packed anion array of the rutile structure transforms first to the HCP array, subsequently cation rearrangement occurs to give a MWO_6 network that is similar

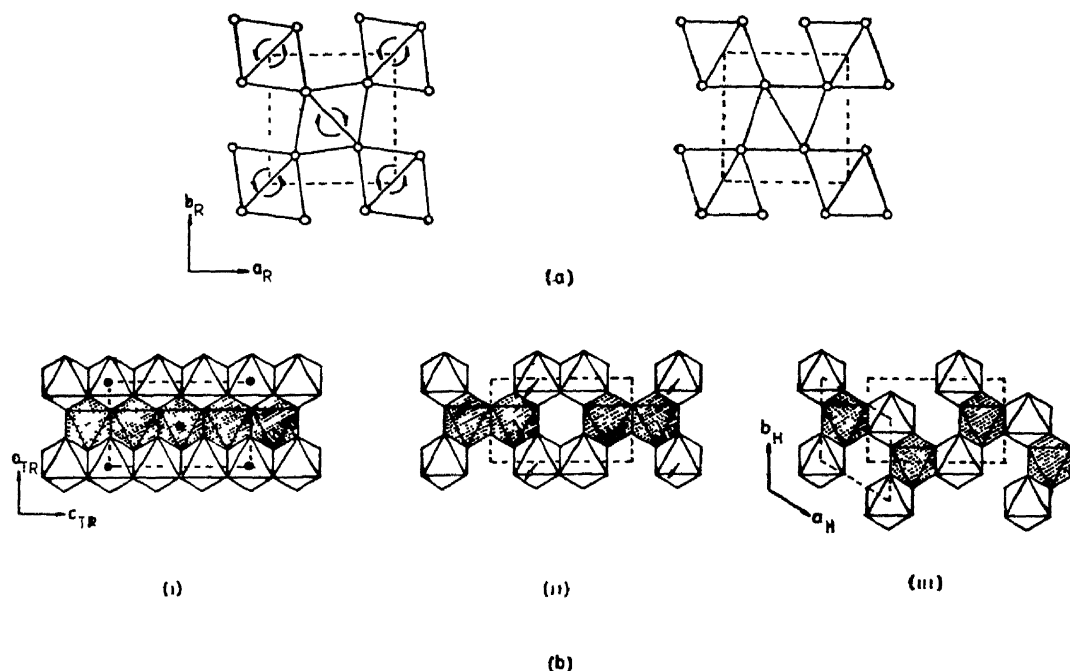


FIG 4 Plausible topochemical mechanism for the transformation of trirutile structure of LiNbWO_6 to ReO_3 structure of HNbWO_6 . (a) shows transformation of tetragonal close packed anion array to hexagonal close packed (HCP) array by rotation of occupied octahedra (b) shows rearrangement of NbWO_6 framework in trirutile to that of NbO_3 in LiNbO_3 . (i) LiNbWO_6 trirutile; Li-occupied octahedra are shown with a filled circle (ii) NbWO_6 framework after removal of lithium (iii) NbWO_6 framework after rearrangement to LiNbO_3 structure.

to the NbO_3 network in the LiNbO_3 structure. The network may then transform to the ReO_3 structure by a mechanism similar to that proposed by Rice and Jackel²² for the transformation of LiNbO_3 to HNbO_3 . The latter involves rotation of the octahedra by $\sim 60^\circ$ about the c_H which rearranges the hexagonal close packed anion array to 3/4 cubic close packed anion array of the ReO_3 structure. We believe that this is the first instance of a transformation of a rutile structure to ReO_3 structure, occurring topochemically on ion-exchange at low temperatures.

Topochemical Delithiation

Reversible topochemical insertion/extraction of lithium and sodium into/from layered metal oxides and chalcogenides has been extensively investigated in view of the importance of such systems as positive electrode materials in high-energy density solid state batteries.²⁵ Insertion/extraction of alkali metal atoms can also be achieved chemically through suitable reducing/oxidizing agents and this offers an attractive route for the synthesis of solids.²⁶ Thus extraction of lithium from LiVS_2 using $\text{I}_2/\text{CH}_3\text{CN}$ has enabled the synthesis of metastable VS_2 .²⁷ We have investigated the topochemical extraction of lithium from LiVO_2 ²⁸ and Li_2MoO_3 . Both the oxides crystallize in layered structures related to rocksalt (Fig 5).

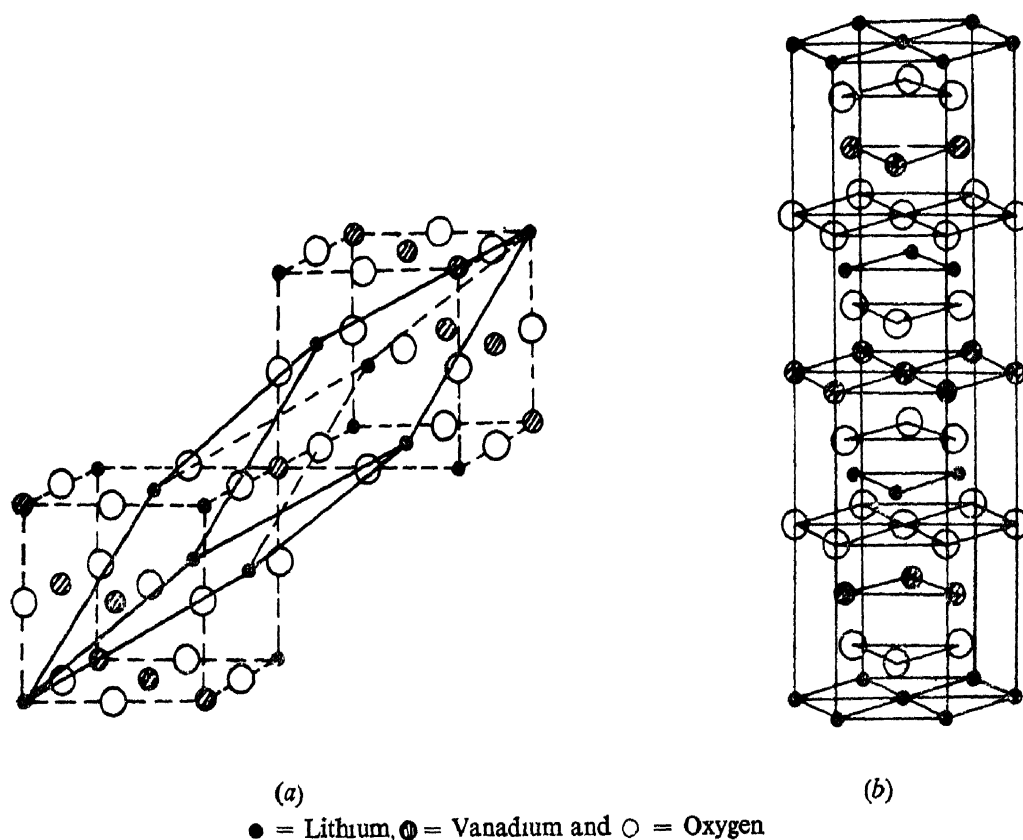
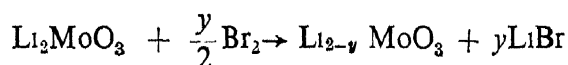
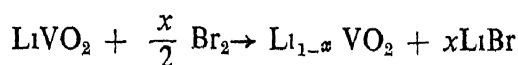


FIG 5 Structure of LiVO_2 (a) shows ordering of Li^+ and V^{3+} in alternate (111) cation planes of the rocksalt structure, (b) hexagonal unit cell of LiVO_2 . Li_2MoO_3 possesses essentially the same structure except that V^{3+} -planes are replaced by planes containing both Li^+ and Mo^{4+} in the ratio 1:2.

In LiVO_2 which adopts the $\alpha\text{-NaFeO}_2$ structure, Li^+ and V^{3+} ions are ordered in alternate (111) cation planes of the rocksalt structure, while in Li_2MoO_3 , entirely Li^+ containing cation planes alternate with those containing Li and Mo in the ratio 1:2.

We have been able to extract lithium from LiVO_2 and Li_2MoO_3 using Br_2 in CHCl_3 as oxidizing agent



In both the cases, delithiation proceeds topotactically yielding $\text{Li}_{1-x}\text{VO}_2$ and $\text{Li}_{2-y}\text{MoO}_3$ series of oxides (Figs 5 and 6). Extent of delithiation can be easily followed by determining the oxidation states of the transition metal ion. In $\text{Li}_{1-x}\text{VO}_2$, there is a marked decrease in c and a slight increase in a as x increases (Table II). The diffraction pattern of $\text{Li}_{1.0}\text{VO}_2$ (Fig 6) is indexable on a cubic unit cell with $a = 8.17\text{\AA}$. The changes in X-ray diffraction patterns of $\text{Li}_{1-x}\text{VO}_2$ are indicative

TABLE II

Chemical compositions and unit cell parameters of $\text{Li}_{1-x}\text{VO}_2$ and $\text{Li}_{2-y}\text{MoO}_3$ obtained by topochemical delithiation

Composition	Oxidation state of V/Mo	Lattice parameters(Å)	
		a_H	c_H
LiVO_2	3.00	2.84	14.79
$\text{Li}_{0.65}\text{VO}_2$	3.35	2.84	14.80
$\text{Li}_{0.45}\text{VO}_2$	3.55	2.86	14.54
$\text{Li}_{0.25}\text{VO}_2$	3.75	2.89	14.31
$\text{Li}_{0.1}\text{VO}_2$	3.90	2.89	14.24
Li_2MoO_3	4.00	2.88	14.93
$\text{Li}_{1.3}\text{MoO}_3$	4.70	2.89	14.94
$\text{Li}_{0.85}\text{MoO}_3$	5.05	2.91	14.89
$\text{Li}_{0.5}\text{MoO}_3$	5.46	2.93	14.77

of a cation rearrangement while retaining the anion subarray de Picciotto *et al.*²⁹ who have investigated the system subsequently have found structural evidence for the rearrangement of vanadium atoms, in $\text{Li}_{0.22}\text{VO}_2$ approximately one-third of the vanadium atoms is located in octahedral sites left vacant in the lithium layer. $\text{Li}_{1-x}\text{VO}_2$ members formed by delithiation appear to be metastable, thus rocksalt-like $\text{Li}_{0.5}\text{VO}_2$ transforms to LiV_2O_4 spinel and a VO_2 obtained by nearly complete delithiation of LiVO_2 transforms to the monoclinic (rutile-type) VO_2 at high temperatures (Fig. 6)

In the $\text{Li}_{2-y}\text{MoO}_3$ system, delithiation proceeds readily up to $y = 1.5$ yielding $\text{Li}_{0.5}\text{MoO}_3$ as the final product. All the intermediate phases up to $y = 1.5$ retain the parent structure (Fig. 7). Complete removal of lithium is not achieved under the conditions employed. It appears that lithium ions present in alternate (111) cation planes are removed while those present in the planes along with molybdenum are not readily extracted. It should be interesting to determine the structure of $\text{Li}_{0.5}\text{MoO}_3$ which would reveal whether cation rearrangement occurs or not.

Topochemical Reduction

Topochemical redox reactions are well known, typical examples being the transformation of iron oxides between rocksalt and spinel structures.⁵ Reduction of WO_3 to yield $\text{W}_n\text{O}_{3n-1}$ and $\text{W}_n\text{O}_{3n-2}$ series of crystallographic shear phases may also be regarded as topotactic process since the relationship to the parent ReO_3 structure can be traced in the products. Similar topotactic reduction of perovskite oxides has not been investigated extensively, although a large number of superstructures derived from anion vacancy ordering in perovskite oxides is known.³⁰ Reduction of CaMnO_3 to $\text{Ca}_2\text{Mn}_2\text{O}_5$ has been found to be a topotactic reaction.³¹

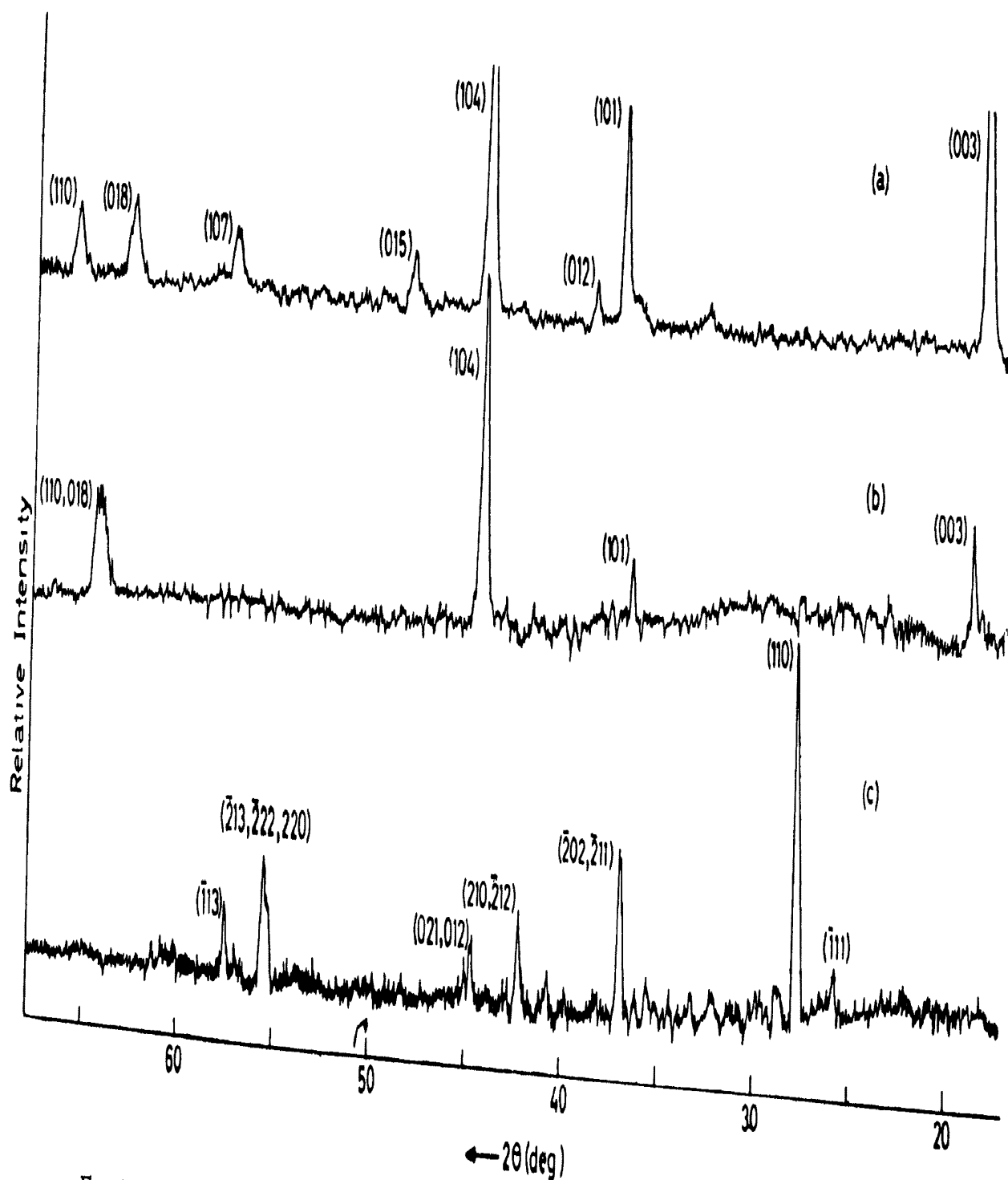
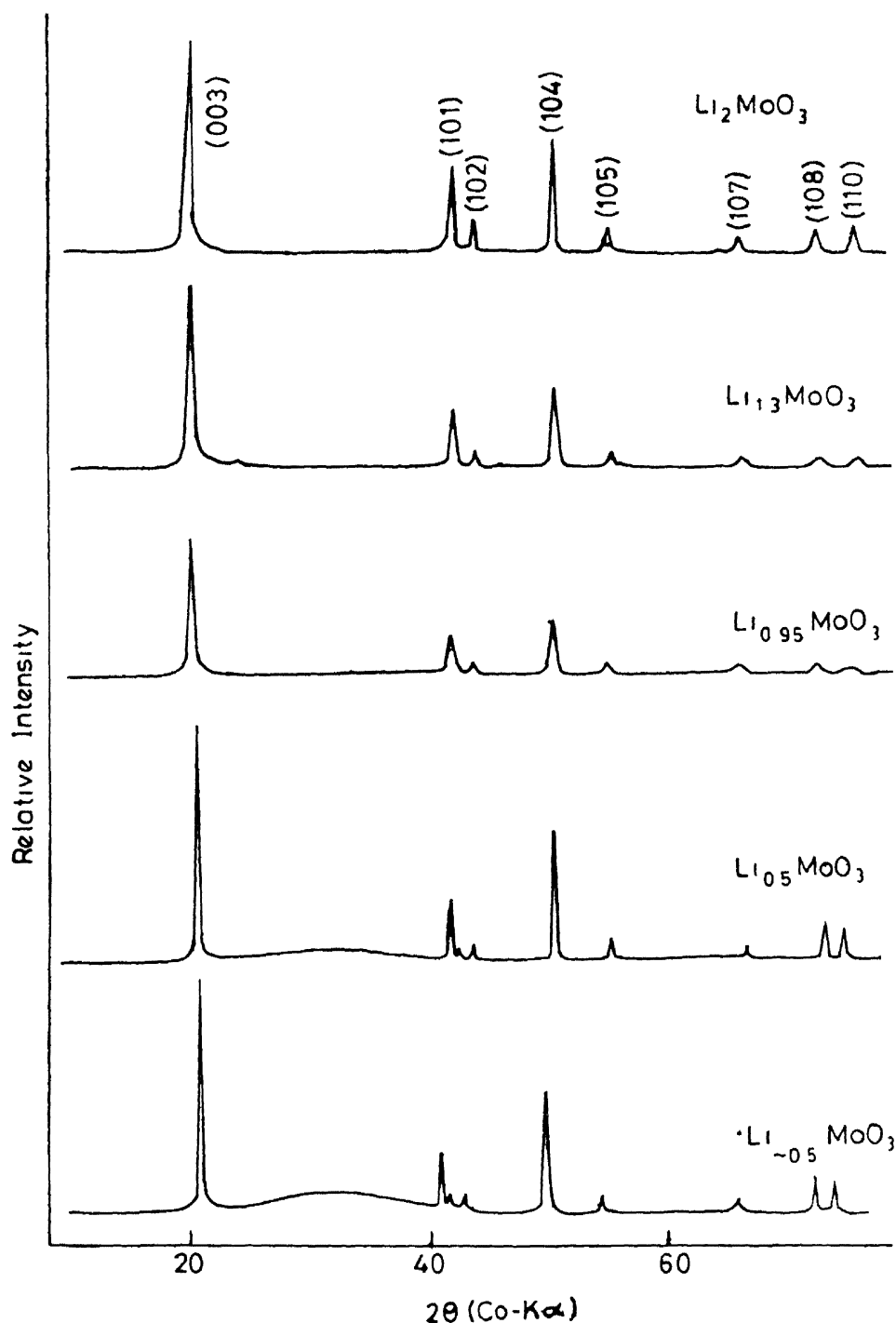


FIG 6 X-ray powder diffraction patterns of (a) LiVO_3 , (b) $\text{Li}_{0.1}\text{VO}_3$ and (c) monoclinic VO_2 ($\text{CuK}\alpha$ radiation)

FIG 7 X-ray powder diffraction patterns of $\text{Li}_{2-x}\text{MoO}_3$

Gai and Rao³² who have investigated the nonstoichiometry of LaNiO_3 by thermogravimetry have proposed the formation of $\text{La}_n\text{Ni}_n\text{O}_{3n-1}$ series. We have recently investigated the reduction of LaNiO_3 and LaCoO_3 under controlled conditions³³. We have found that the reduction proceeds to give metastable phases of composition $\text{La}_2\text{Ni}_2\text{O}_5$ and $\text{La}_2\text{Co}_2\text{O}_5$. What is interesting is that both the oxides can be oxidized back to the parent perovskites indicating that the reversible reduction-oxidation is

indeed a topochemical reaction. X-ray and electron diffraction data (Figs 8 and 9) reveal that while $\text{La}_2\text{Co}_2\text{O}_5$ adopts a brownmillerite structure, $\text{La}_2\text{Ni}_2\text{O}_5$ exhibits a new type of anion vacancy ordering in the perovskite structure involving octahedral and square-planar coordination of Ni^{2+} . The difference between the structures of compositionally similar $\text{La}_2\text{Ni}_2\text{O}_5$ and $\text{La}_2\text{Co}_2\text{O}_5$ can be attributed to the differences in site preferences of Co^{2+} and Ni^{2+} , when the ions are forced to accept four-fold anion coordination, Co^{2+} would prefer a tetrahedral geometry while Ni^{2+} would favour a square-planar geometry.

Topochemical Insertion of Hydrogen and Bismuth in Transition Metal Oxides

Hydrogen atoms can be inserted topotactically into a variety of inorganic solids.⁷ Insertions of hydrogen into MoO_3 and MnO_2 yielding H_xMoO_3 and H_xMnO_2 are some of the early examples of this type of reaction.^{34,35} Hydrogen insertion is a redox process involving electron transfer from the hydrogen atom to the reducible cation of the host solid. Hydrogen insertion has so far been investigated mainly with the binary transition metal oxides such as WO_3 , MoO_3 , ReO_3 and V_2O_5 . We have found that hydrogen can be readily inserted into LaNiO_3 and LaCoO_3 perovskites at low temperatures in the presence of platinum which acts as a hydrogen-spillover catalyst. The compositions of the insertion compounds are $\text{H}_{0.85}\text{LaNiO}_3$ and $\text{H}_{0.50}\text{LaCoO}_3$ as determined by chemical analysis of oxidation states of nickel and cobalt. The insertion products possess essentially the same perovskite structure as the parent material (Fig 10) with a slight increase in lattice parameter (pseudocubic unit cell parameter of $\text{H}_{0.85}\text{LaNiO}_3$ is 3.880 Å, while the corresponding value for LaNiO_3 is 3.826 Å). The hydrogen insertion compounds exhibit a much higher resistivity than the parent perovskites. Thus, while the resistivity of a compressed pellet of LaNiO_3 at room temperature was around 1 ohm cm, the resistivity of the same pellet after hydrogen insertion was $\sim 10^4$ ohm cm. These results are consistent with the reduction of the transition metal ions to the divalent state on hydrogen insertion. Further work is in progress to characterize the structure and properties of hydrogen-insertion compounds derived from perovskite oxides.

We have been able to insert hydrogen into HMWO_6 ($M = \text{Nb}$ or Ta) as well as in $\text{Mo}_{1-x}\text{W}_x\text{O}_3$ using Pt as the catalyst. $\text{H}_{1-x}\text{MWO}_6$ ($x \sim 0.3$) phases are isostructural with the parent HMWO_6 adopting cubic ReO_3 -type structure. The phases are deep blue in colour and exhibit a much lower resistivity (~ 30 ohm cm) than the parent oxides ($\sim 10^6$ ohm cm). The blue colour and the low resistivity reveal partial reduction of W^{6+} to W^{5+} on hydrogen insertion. With $\text{Mo}_{1-x}\text{W}_x\text{O}_3$, hydrogen insertion results in an increase of the symmetry of the structure, becoming tetragonal and cubic with increasing hydrogen content. Powder diffraction patterns of $\text{Mo}_{0.5}\text{W}_{0.5}\text{O}_3$ and $\text{H}_{0.2}\text{Mo}_{0.5}\text{W}_{0.5}\text{O}_3$ are compared in Fig 11. The pattern of the hydrogen insertion compound can be indexed on a tetragonal cell with $a = 5.210$ and $c = 3.91$ Å.

WO_3 forms a variety of tungsten oxide bronzes, A_xWO_3 ($A =$ electro-positive metal) which can be regarded as insertion compounds.³⁶ The structures

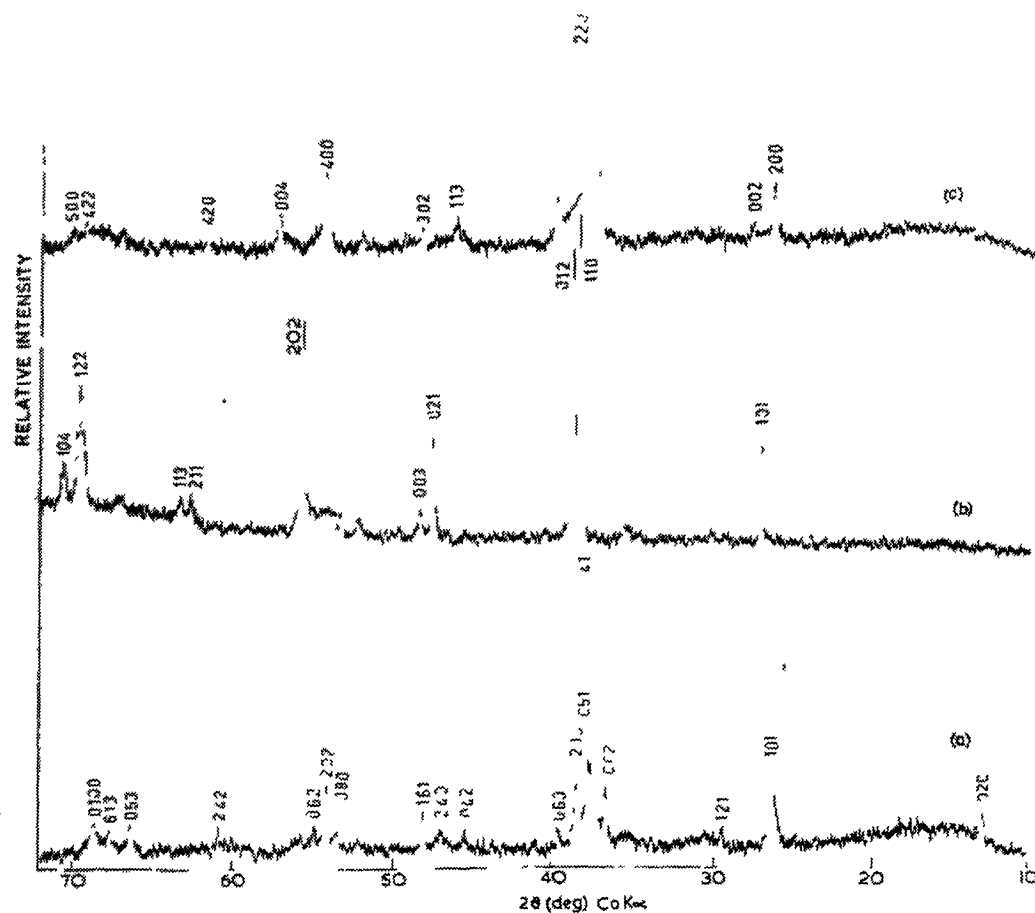


FIG 8 X-ray powder diffraction patterns of (a) $\text{La}_2\text{Co}_2\text{O}_7$, (b) LaCoO_3 , obtained by oxidizing $\text{La}_2\text{Co}_2\text{O}_5$, and (c) $\text{La}_2\text{Ni}_2\text{O}_7$.

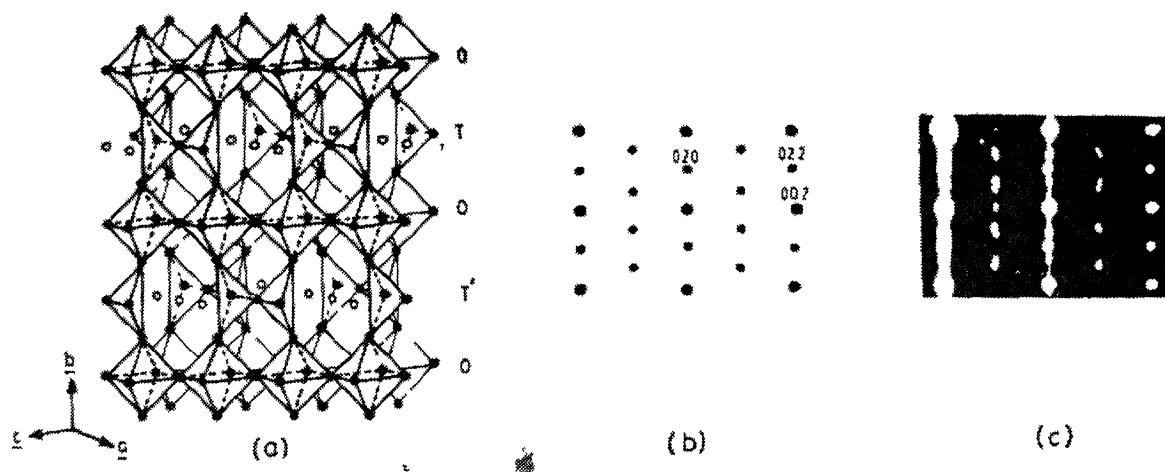


FIG 9 The structure and electron diffraction pattern of $\text{La}_2\text{Co}_2\text{O}_7$ in [100] zone axis—(a) brownmillerite structure, (b) the diffraction pattern expected and (c) the diffracted pattern observed

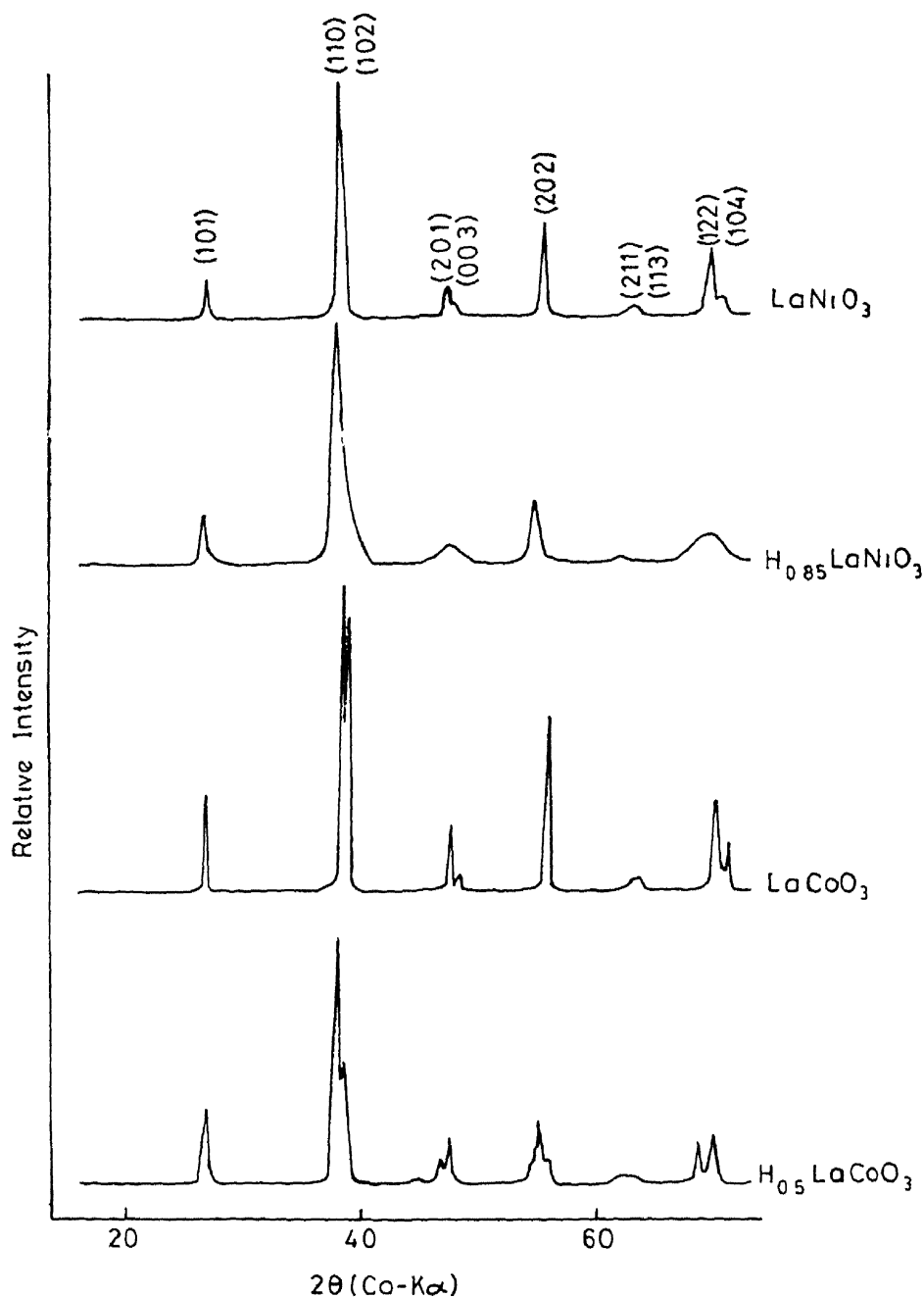


FIG 10 X-ray powder diffraction patterns of LaNiO_3 , LaCoO_3 , and their hydrogen insertion products

of these compounds depend on the identity of A as well as the value of λ . In addition to the three well-known tungsten bronzes, viz., cubic (perovskite-like), tetragonal (TTB) and hexagonal (HTB), a new type of tungsten bronze, called intergrowth tungsten bronze (ITB), has been discovered for small λ values of A = K, Rb or Cs³⁷. We have found that reaction of bismuth with WO_3 in sealed tubes around 900 °C results in insertion of bismuth atoms into WO_3 , yielding ITBs, $\text{Bi}_\lambda\text{WO}_3$ ($\lambda \leq 0.07$). Detailed investigations of $\text{Bi}_\lambda\text{WO}_3$ have shown that each bismuth transfers three electrons to the WO_3 host^{11a}. The intergrowth structure of

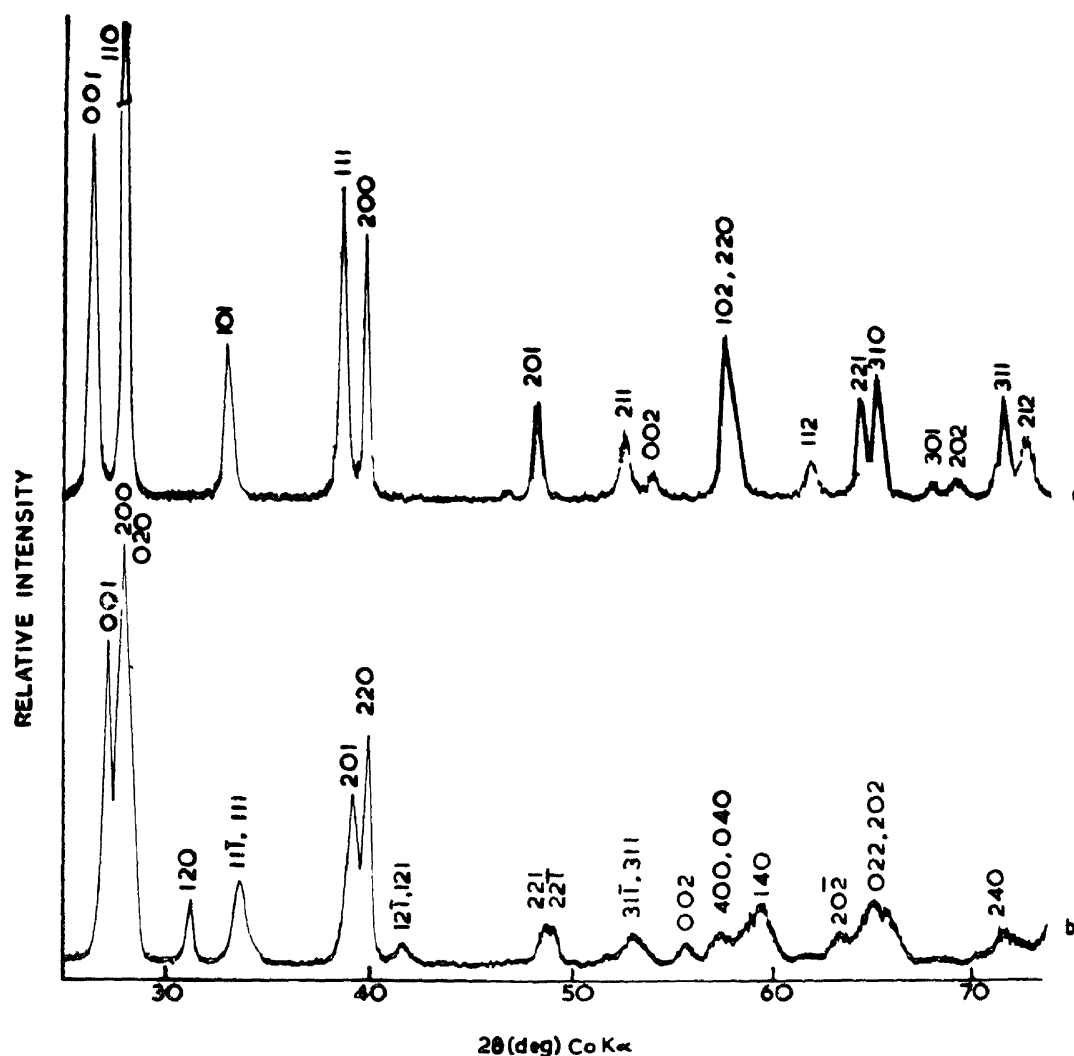


FIG 11 X-ray powder diffraction patterns of (a) $\text{Mo}_{0.5}\text{W}_{0.5}\text{O}_3$ and (b) $\text{H}_{0.2}\text{Mo}_{0.5}\text{W}_{0.5}\text{O}_3$

the bronzes, consisting of slabs of WO_3 strips of HTB units, one tunnel wide, has been revealed by high resolution electron microscopy (Fig 12). Formation of the ITB structure can be viewed as a topochemical process since insertion of bismuth rearranges the octahedral network of the parent WO_3 to produce hexagonal tunnels to accommodate bismuth without breaking the W-O bonds in the parent oxide.

CONCLUDING REMARKS

The results reported in the paper show that it is possible to exploit topochemical reactions of inorganic solids, which occur at relatively low temperatures, to design new strategies for the synthesis of metal oxides. It should be interesting to extend topochemical methods for the synthesis of other classes of inorganic solids such as metal halides and metal chalcogenides. Synthesis of VS_2 by extraction of lithium from LiVS_2 , of MFe_2S_4 ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) starting from KFeS_2 by ion-exchange and of Mo_6S_8 from $\text{Cu}_x\text{Mo}_6\text{S}_8$ by acid leaching are some of the examples of topochemical synthesis of metal sulphides.^{27, 38} The significance of the present

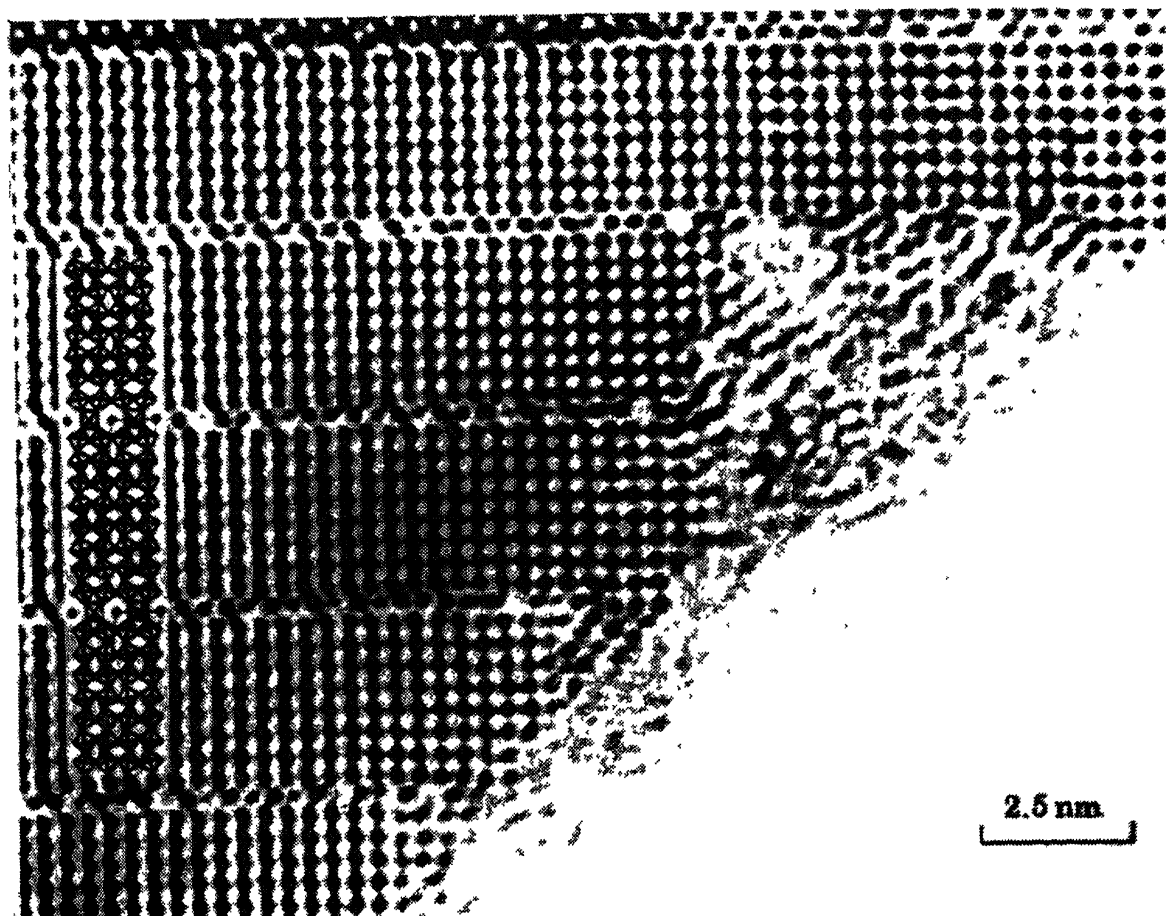


FIG 12 High resolution electron microscope (500 kV) image of $\text{Bi}_{10}\text{WO}_{19}$ revealing the ITB structure. Slabs of WO_3 and HTB strips where Bi atoms are located are clearly seen in the image ^{11a}

work extends beyond solid state synthesis. It is not known, for instance, why in some topochemical reactions the structure is essentially retained, while a structural transformation accompanies the reaction in others, as in the case of conversion of LiNbO_3 to HNbO_3 . The role of electronic configuration of the transition metal atom and the nature of bonding in the solid on the course of topochemical reactions are not clear at present. Thus it is not known why LiNbO_3 undergoes facile proton-exchange in aqueous acids, while the structurally related LiSbO_3 does not. Similarly, it is not known why lithium insertion into ReO_3 giving LiReO_3 and Li_2ReO_3 is accompanied by a structural transformation³⁹ while a similar transformation is not seen when lithium is extracted from Li_2MoO_3 . These aspects deserve further investigation.

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NUMEROUS STRUCTURES OF OXIDES CAN BE BUILT UP FROM THE ReO_3 -TYPE FRAMEWORK

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Key Words : Oxide Structures; ReO_3 -Type Framework; Aurivillius Phase; Perovskite

INTRODUCTION

THE perovskite structure, or more exactly the ReO_3 -type lattice forming this structure is one of the most fascinating frameworks owing to its great simplicity and flexibility Galasso,¹ Wells² and Rao *et al*³ have shown that the perovskite structure is involved in a great number of oxides. Moreover it appears, from the latter review that many structures are related to the perovskite. The aim of the present paper is to analyze the " MO_3 " framework and to show that it can be used as a precursor for generation of new structural families, and also that some structures which are known since a long time are in fact closely related to the " MO_3 " host-lattice.

THE ReO_3 -TYPE HOST-LATTICE

The consideration of the ReO_3 structure (Fig. 1a) or of the cubic ABO_3 perovskites (Fig. 1b) shows that they are both formed of the same octahedral framework MO_3 . This host lattice can be described as built up from " M_4O_{20} " units forming square tunnels (Fig. 2a) connected through the corners of their octahedra (Fig. 2b). The only difference between ReO_3 and the cubic perovskite concerns the occupancy of the tunnels which are empty in ReO_3 and fully occupied in the stoichiometric ABO_3 perovskites, while a partial and random occupancy is possible as shown in the bronzes A_xWO_3 for $A = \text{Li}, \text{Na}, \text{Ln}, \text{Ca}, \text{Sr}, \text{U}, \text{Cd}, \text{Hf}$ (for review see ref. 4-6). A great number of stoichiometric perovskites exhibit a distorted MO_3 host-lattice which corresponds to a deformation of the MO_6 octahedra.¹ Another way of distorting the MO_3 framework corresponds to its compression or elongation along one [100] direction: it results in diamond-shaped " M_4O_{20} " units (Fig. 3) in which the MO_6 octahedra may remain regular. Many diamond shaped-tunnel perovskites⁷⁻¹¹ have been recently isolated involving Jahn-Teller ions such as Cu^{2+} and Mn^{3+} . It is for instance the case of the oxides $[\text{CaCu}_3]_A\text{M}_4\text{O}_{12}$ ($M = \text{Ti}, \text{Mn}$) and $[\text{CaMn}_3]_A\text{Mn}_4\text{O}_{12}$ in which three A sites out of four are occupied by the Jahn Teller ions in an ordered way, and of the defect perovskites $(\text{Cu} \square)_A\text{Ta}_2\text{O}_6$ and $(\text{Mn} \square)_A\text{Mn}_4\text{O}_{12}$ in which vacancies and Jahn-Teller ions are distributed in an ordered way on the A sites. Those cubic perovskites whose " a " parameter is twice that of the ideal

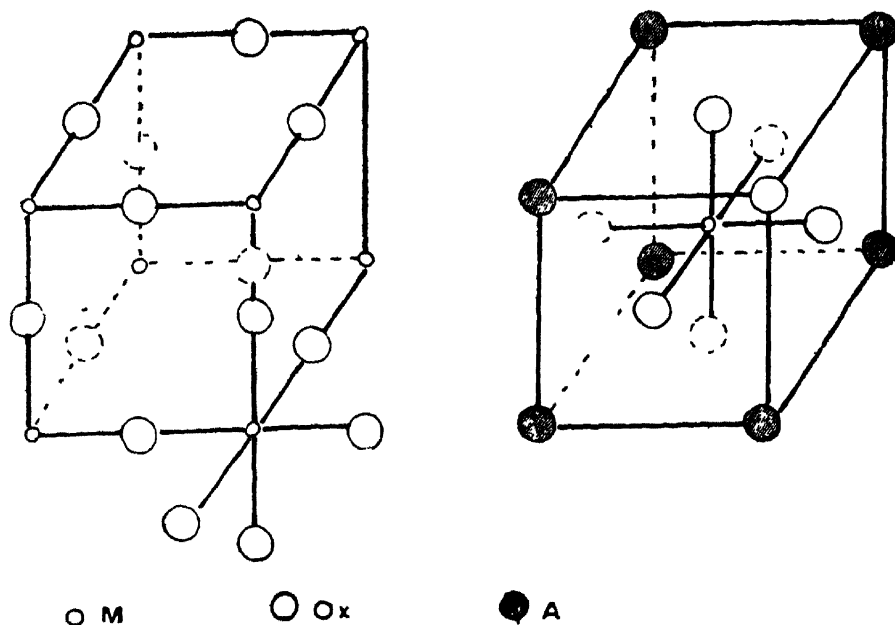


FIG 1 The usual representation of the ReO_3 -structure (a) and of the perovskite structure AMO_3 (b)

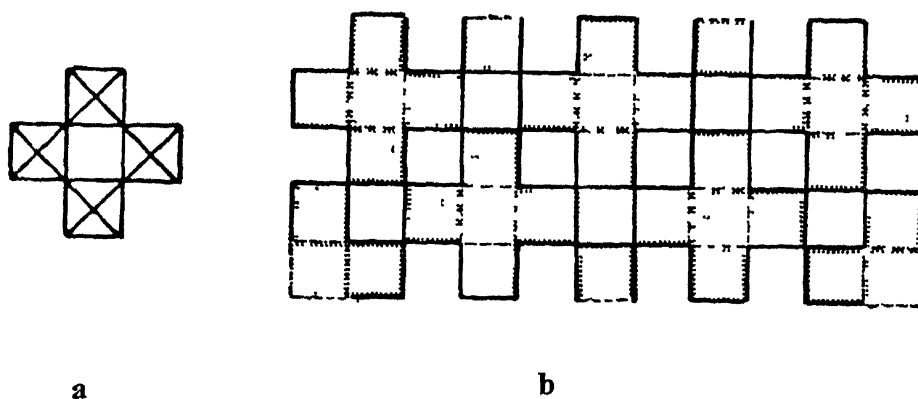
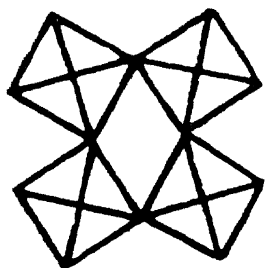
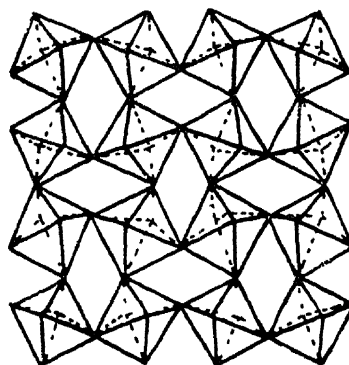
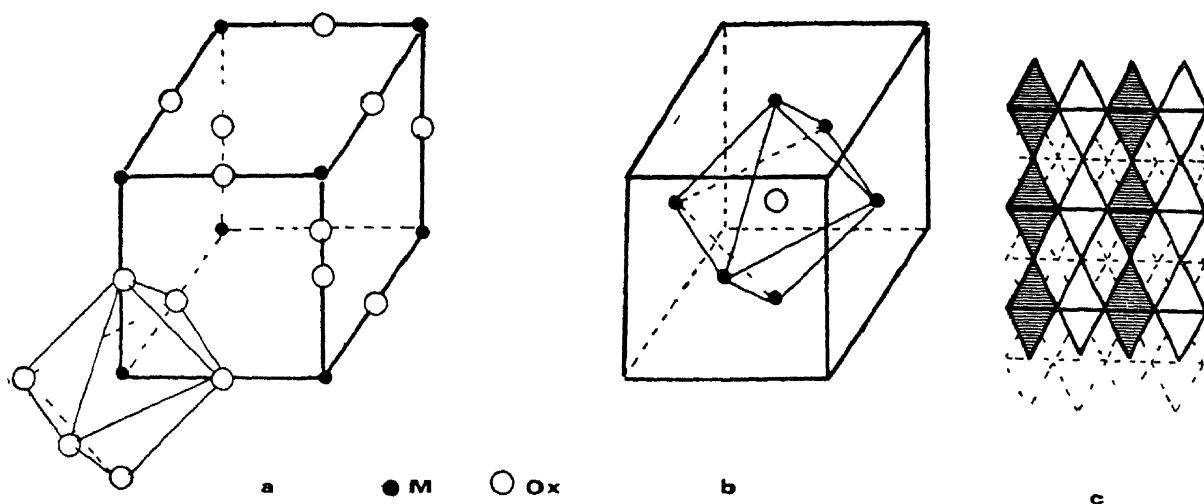


FIG 2 The octahedral " M_4O_{20} " units forming square tunnels (a) and their connection forming the MO_3 framework (b)

perovskite result from a compression of the ideal MO_3 framework and a tilting of the MO_6 octahedra (Fig 4). This effect is a consequence of the presence of the Jahn-Teller ions Cu^{2+} or Mn^{3+} which take no more a 12-fold but a square planar coordination

Thus it appears that the square " M_4O_{20} " units and the diamond shaped " M_4O_{20} " units are the two extreme units which can participate to the formation of the " MO_3 " perovskite host-lattice. Consequently, one can imagine that the great ability of deformation of the perovskite " MO_3 " framework without a sensible distortion of the MO_6 octahedra, should allow a great adaptability to various frameworks and polyhedra and to generate new structures closely related to perovskite


FIG 3 The diamond-shaped " M_4O_{20} " units

FIG 4 The diamond-shaped $\text{CaCu}_3M_4\text{O}_{13}$ -perovskite.

FIG 5 Description of the sodium chloride type structure of the MO oxides (a) the $[\text{MO}_3]^{4-}$ ReO_3 -type framework (b) the anti- ReO_3 $[\text{OM}_3]^{4+}$ framework and (c) interpenetration of the two octahedral frameworks

THE ADAPTABILITY OF THE ReO_3 -TYPE FRAMEWORK TO OTHER OCTAHEDRAL STRUCTURES

The ReO_3 -Lattice and the Sodium Chloride Structure

A very well-known structure, which is often the first structure taught to the students is the one of sodium chloride owing to its cubic face centered character involving an ABC close-packing of the anions and of the cations. In fact, this structure is rather complex and derives from the ReO_3 -framework. The examination of the MO sodium chloride type oxides shows that a quarter of the metallic M atoms and three quarters of the oxygen atoms form a ReO_3 -type lattice built up from corner-sharing MO_6 octahedra (Fig 5a), whereas the remaining M and oxygen atoms form a OM_3 lattice built up of corner-sharing OM_6 octahedra (Fig 5b) whose dimensions are identical to those of the MO_6 octahedra. Thus it appears that the MO -sodium chloride structure is composed of two interpenetrated and isometric $[\text{MO}_3]^{4-}$ and $[\text{OM}_3]^{4+}$ frameworks (Fig 5c) the first one exhibits the ReO_3 structure whereas the second is an anti- ReO_3 framework.

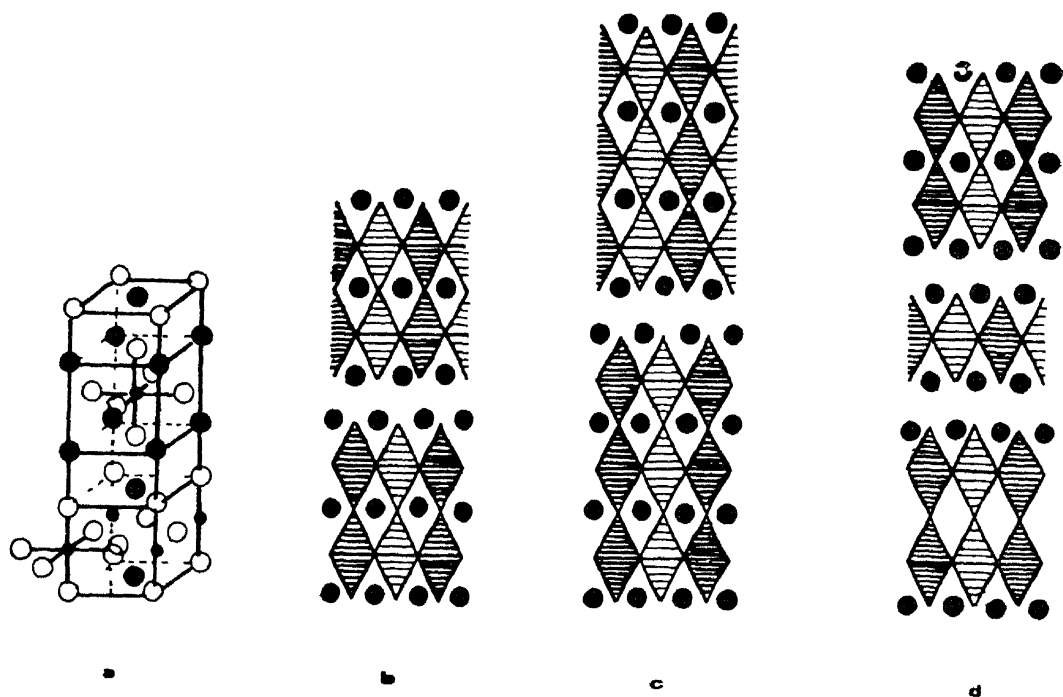


Fig 6 Structure of the intergrowths between perovskite and sodium chloride type oxides $(AO)(AMo_3)_n$: structure of the K_2NiF_4 -type, $n = 1$ (a) and schematic representations of the members $n = 2$ (b), $n = 3$ (c) and $n = 1.5$ (d)

The close relationship of the perovskite structure with the sodium chloride structure is also clearly visible by considering the "AO" planes of the AMo_3 perovskite at the level $z = 0$ (Fig. 1b) which are characterized by sodium chloride type arrangement of the A and O ions. A consequence of this bidimensional accord between the AO rock salt structure and the AMo_3 perovskite leads to the generation of intergrowths $AO (AMo_3)_n$.^{5,12-20} These phases consist of single sodium chloride type layers alternating with multiple perovskite layers, which are n octahedra thick (Fig. 6). Several series of oxides $AO (AMo_3)_n$ have been synthesized for $A = Ca, Sr, Eu^{II}$ and $M = Mn, Ti$, many oxides exhibit the K_2NiF_4 structure which corresponds to the first number of the series La_2CuO_4 , La_2NiO_4 , Sr_2MO_4 ($M = Ti, Sn, Mn, Mo, Rn, Ir, Rh$), Ba_2MO_4 ($M = Sn, Pb$), A_2UO_4 ($A = K, Rb, Cs$). The order between the AO and AMo_3 layers decreases as the thickness of the perovskite layers increases so that for very high n ($n \rightarrow \infty$) values the AO layers appear in the form of bidimensional defects in the perovskite matrix. Moreover, it must be pointed out that for non-integral n values multiple intergrowths corresponding to a sequence of several different perovskite layers (Fig. 6d) may be obtained, however, such intergrowths have never been observed in the ordered state.

*The Diamond-shaped ReO_3 -Framework and the Hexagonal Tungsten Bronze Structure (HTB)*²¹⁻³²

The comparison of the idealized diamond-shaped ReO_3 host-lattice (Fig. 7a) and of the HTB A_xWO_3 (Fig. 7b) shows that these two structures are formed of

identical octahedral layers characterized by angles of 60 and 120°. The intergrowth of these structural types, can be realized by means of these layers (Fig. 7c). Thus, a series of bronzes $A_x\text{WO}_3$ ($A = \text{K, Rb, Tl, Cs, Sn, Pb, Sb}$) called intergrowth tungsten bronzes (ITB), and dielectric oxides $A_xM_x\text{W}_{1-x}\text{O}_3$ ($A = \text{K, Rb, Tl, Cs}$) called bronzoids were isolated. Fig 7c shows as an example the structure of one of these ITB's observed for the bronzoids $\text{Cs}_x(\text{Nb}_x\text{W}_{1-x})\text{O}_3$. Several ordered ITB's in which the HTB and diamond shaped perovskite slabs exhibit different thicknesses were isolated. Many disordered intergrowths were observed. Most of the ITB's are characterized by the presence of tungsten in the MO_3 framework, except for $\text{Sb}_{0.2}\text{MoO}_{3.1}$, $\text{Ca}_2\text{TlTa}_5\text{O}_{15}$ and the oxides $\text{ACu}_3\text{M}_7\text{O}_{21}$ ($A = \text{K, Rb, Tl, Cs}$ and $M = \text{Nb, Ta}$).³⁰ The copper compounds are rather different from the other ITB's (Fig. 8) in that the Cu^{2+} ions which exhibit a square planar coordination are located in the diamond-shaped perovskite tunnels, the realisation of such a coordination for copper necessitates a tilting of the MO_6 octahedra along the c -direction perpendicular to the plane of the projection involving a doubling of the c -parameter with respect to the other ITB's. As a consequence this latter structure must be considered as modified ITB's, resulting from the intergrowth of the diamond shaped perovskite $\text{Cu}_3 \square \text{M}_4\text{O}_{12}$ and of the HTB's AM_3O_9 . It is clear that such an intergrowth is initiated by the Jahn-Teller effect of copper

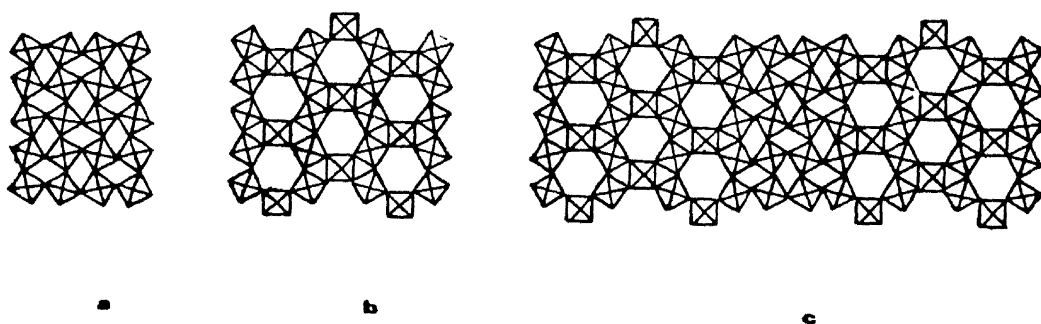


FIG 7 The idealized MO_3 host lattice (a) and the HTB framework (b) and the ITB $\text{Cs}_x(\text{Nb}_x\text{W}_{1-x})\text{O}_3$ (c)

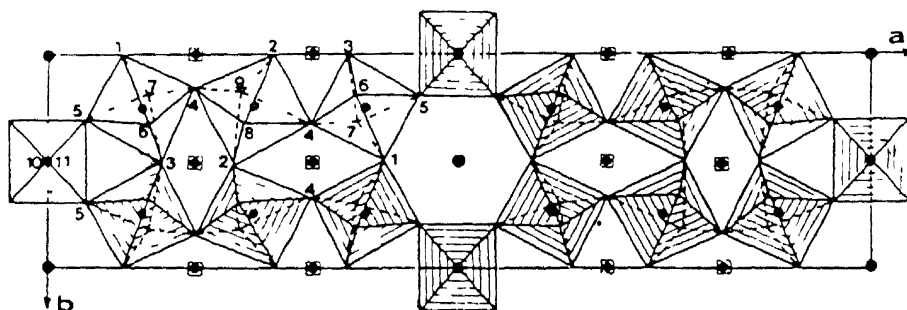


FIG 8 The modified ITB $\text{ACu}_3\text{M}_7\text{O}_{21}$, intergrowth of the diamond shaped perovskite $\text{Cu}_3 \square \text{M}_4\text{O}_{12}$ and of the HTB AM_3O_9

The M_4O_{20} Perovskite Columns and the TTB Structure^{6,33-43}

The MO_3 perovskite framework is closely related to the tetragonal tungsten bronze structure discovered by Magnéli. The rotation of a M_4O_{20} perovskite column in a ReO_3 -type matrix (Fig. 9a) of $\pi/4$, leads to the formation of TTB microregions characterized by four pentagonal tunnels surrounding a square perovskite tunnel. Such an intergrowth is not so easy to realize, owing to the fact that it involves a small distortion of the MO_6 octahedra (Fig. 9b)

The presence of such isolated defects, in the form of TTB columns in the MO_3 -perovskite matrix has been observed by high resolution electron microscopy WO_3 - Nb_2O_5 system for the tungsten-rich compositions. It is obvious that the ordered formation of such "defects" in the ReO_3 -type matrix should lead to a series of microphases. The limit phase is in fact represented by the TTB structure observed for $K_{0.50}WO_3$ (Fig. 9b) and $Nb_8W_9O_{47}$ (Fig. 9c) in which the "rotation defects" are so close to each other that no more place is left for the initial ReO_3 -type matrix. Intermediate structures, which are intergrowths of the TTB and MO_3 -perovskite structures can thus be predicted. The Nb_2O_5 - WO_3 system is a good example in which the TTB- ReO_3 -type intergrowths are easily formed. Fig. 10 shows, for example, the structure of $Nb_8W_{22}O_{86}$ and the formation of the TTB slabs in the ReO_3 -type matrix by ordered rotation of the " M_4O_{20} " units. Such an inter-

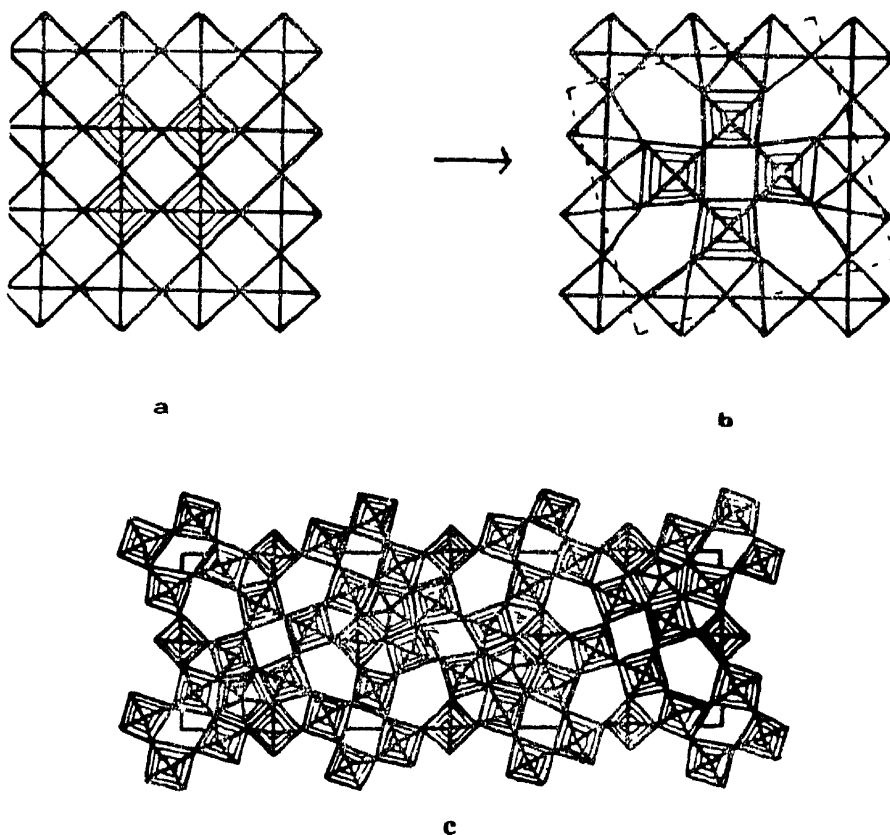


FIG. 9 The rotation of a " M_4O_{20} " unit in a ReO_3 -type matrix (a) leads to a TTB region (b) also observed for $Nb_8W_9O_{47}$ (c).

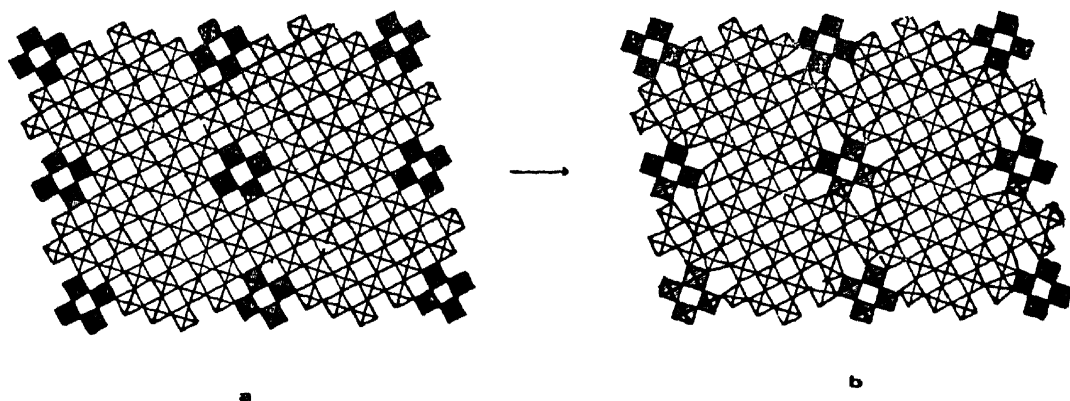


FIG 10 The cooperative rotation of the " M_4O_{20} " units (a) in a ReO₃-type matrix leading to the formation of the TTB slabs (b) in the ReO₃-type matrix

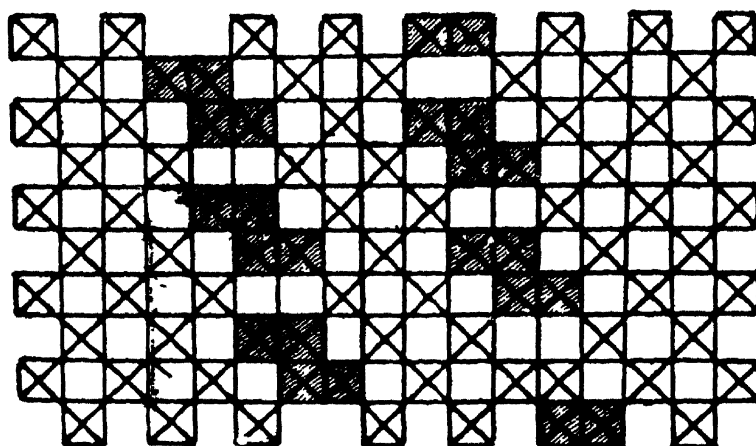
growth can be formulated $[(MO)_2M_{10}O_{30}]^{TTB} [MO_3]_{2n}^{ReO_3}$ with $n = 9$, where n corresponds to the number of octahedra forming the ReO₃-type chains between two TTB slabs and determines the width of the ReO₃-type slabs whereas $(MO)_2$ represents the number of " MO " chains located in the pentagonal tunnels of the TTB slabs. Thus a general formulation $[(MO)_xM_{10}O_{30}]_m^{TTB} [MO_3]^{ReO_3}$, can be proposed for the different ordered intergrowths of this system where m and n are integral numbers corresponding to the width of the TTB and ReO₃-type slabs respectively and x is a non-integral number ($x < 4$) corresponding to the insertion rate of the MO chains in the pentagonal tunnels.

The oxides Nb₈W₂₂O₈₆ and Nb₄W₇O₃₁ correspond to the members $m = 1$ with $n = 9$ and 5 respectively, while Nb₁₂W₁₁O₆₃ is characterized by the values $m = 2$ and $n = 5$.

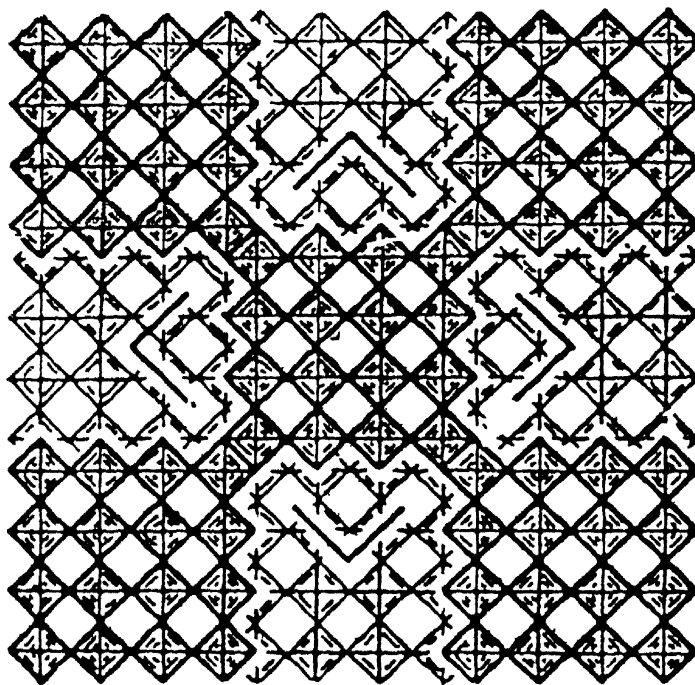
The TTB slabs are frequently disordered with variable widths, involving a wide domain of non-stoichiometry which is amplified by a variable insertion rate in the pentagonal tunnels. Analogous phenomena are observed in the Ta₂O₅-WO₃ system.

SHEAR STRUCTURE DERIVED FROM THE ReO₃-TYPE LATTICE^{2-6,44-66}

The shear-structures derived from the ReO₃-type lattice over a wide field of investigation ranging from the molybdenum and tungsten suboxides M_nO_{3n-1} and M_nO_{3n-2} to the block structures derived from the M , N and H Nb₂O₅ forms. It is not possible to discuss here in a detailed way all those structures owing to their very great number. Examples of a simple shear structure Mo₉O₂₆ and of a block structure M -Nb₂O₅ are presented on Fig 14a and 11b respectively. From their examination it is obvious that they are closely related to the MO₃ framework and derive from the latter by sharing the edges of their octahedra instead of their corners. It must simply be emphasized that the true single shear structures are formed of ReO₃-type slabs separated by infinite crystallographic shear planes (CSP) in which the MO₆



a



b

FIG 11 Structures of a true single shear structure Mo_9O_{26} (a) and of a block-structure $M\text{-Nb}_2\text{O}_5$.

octahedra share their edges, whereas the block structures result from a combination of several shearing phenomena leading no more to perovskite slabs but to MO_3^- perovskite columns sharing the edges of their octahedra

It is well known that the direction of the CSP's in those structure depends on the number of octahedra sharing their edges. The most frequent CSP's $\{102\}$ $\{103\}$ and $\{001\}$ or $\{100\}$ are formed of blocks of 2×2 , 2×3 and $2 \times \infty$ edge-sharing octahedra respectively (Fig. 12). It must be pointed out that these CSP's formed of $2 \times n$ edge-sharing octahedra, are themselves built up from edge-sharing " $M_4\text{O}_{20}$ " units for even- n values (Fig. 12 b and e)

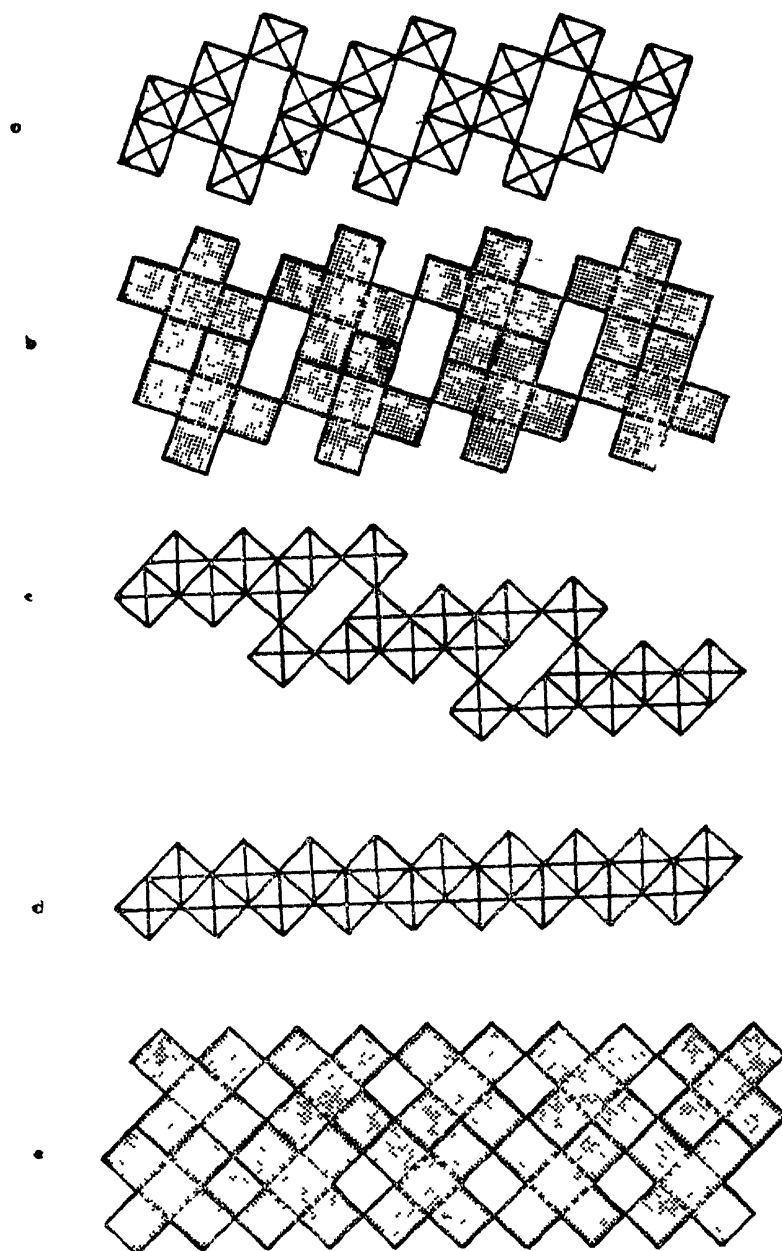


FIG 12 The most current crystallographic shear planes $\{102\}$ (a, b), $\{103\}$ (c), $\{001\}$ (d-e)

Besides the $\{102\}$ and $\{103\}$ C S P which lead to the formation of the M_nO_{3n-1} and M_nO_{3n-2} shear structures respectively, the $\{001\}$ C S P exhibits a particular interest in that they can be formed in two different ways noted $\{001\}^a$ (Fig. 13a) and $\{001\}^b$ (Fig. 13b), leading always to oxides of formulation M_nO_{3n-1} . It results that two other different series of M_nO_{3n-1} can be considered: the oxides characterized by the presence of one type of CSP's only (a or b considered separately are equivalent), and the oxides in which the two types of CSP $\{001\}^a$ and $\{001\}^b$ coexist in the structure. An example of the first series is given by Nb₃O₇F or V₂MoO₈ third member of the series (Fig. 13c) whereas an example of the second series is given by P-Nb₂O₅ (Fig. 13d) second number of the series. It is remarkable that first number of this second series (Fig. 13e) corresponds to a very compact structure

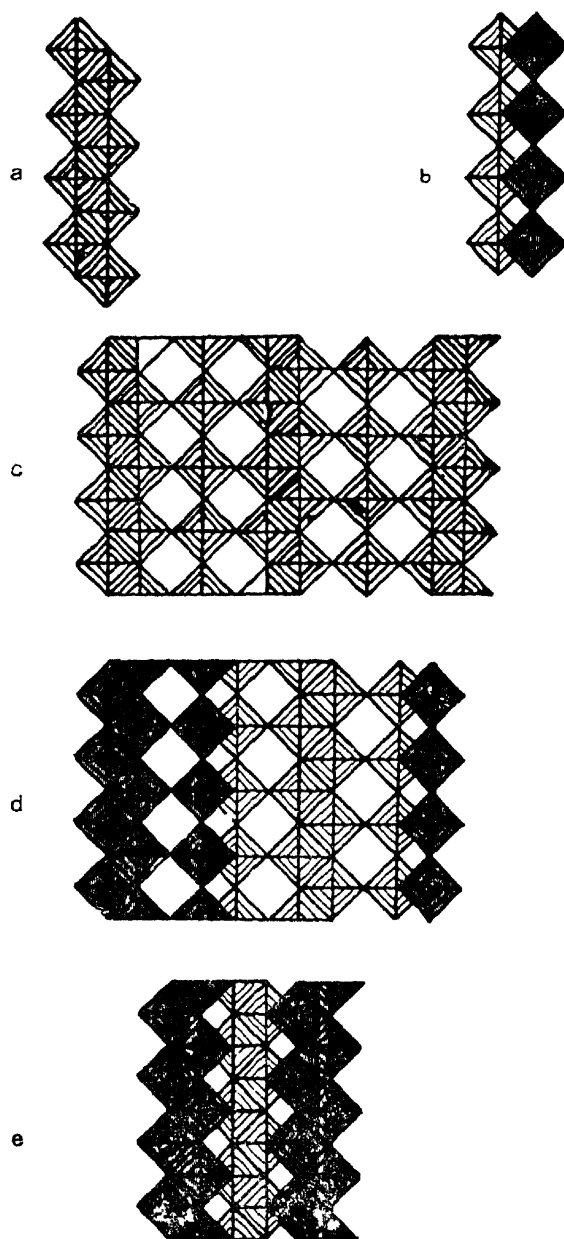


FIG 13 The M_nO_{3n-1} shear structures. The two representations of $\{001\}$ CSP's (a) and (b), comparison of the structure of the oxides V_2MoO_8 (c), $P-Nb_2O_5$ (d) and idealized anatase TiO_2 (e).

only built up from edge-sharing octahedra, this latter structure is in fact observed for the anatase form of TiO_2 with a sensible distortion of the octahedra. Consequently these CS structures can be considered as a result of the adaptability of the ReO_3 -type framework to the MO_2 -anatase structure

LAYER STRUCTURES

The great flexibility of the ReO_3 -type framework makes that the perovskite structure can also be "cut up" in the form of anionic layers whose cohesion is ensured either

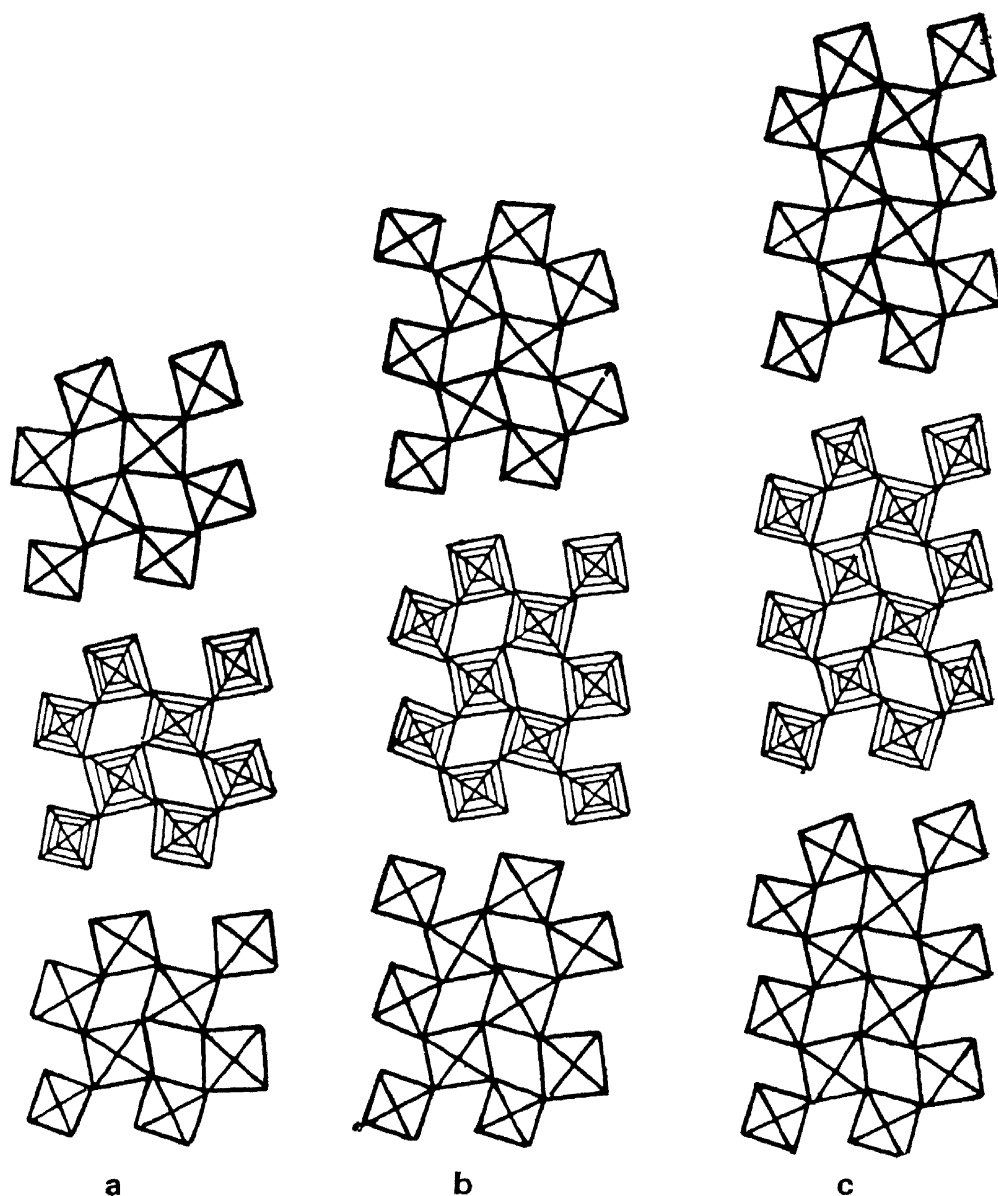


FIG 14 The layer titanates and titanoniobates $A_nM_nO_{3n+2}$ $n = 4$ (a), $n = 5$ (b) and $n = 6$ (c)

by A^{2+} ions like in the layer oxides $A_nM_nO_{3n+2}$ or by infinite cationic layers $[B_{12}O_2]_n^{2n+}$ like in the Aurivillius phases

*The Titanates and Titanoniobates $A_nM_nO_{3n+2}$ with a Layer Structure*⁶³⁻⁶⁷

These compounds form a very important family in which A is an alkaline-earth ion and or a lanthanide ion and M is titanium and or niobium. The different members of the series were isolated in the systems $A_2Nb_2O_7$ - $CaTiO_3$ ($A = Ca, Sr$) and $Ln_2Ti_2O_7$ - $CaTiO_3$ ($Ln = La, Nd$). Their structure consists of infinite anionic layers $[M_nO_{3n+2}]^{n'-}$ ($2n \leq n' \leq 3n$), whose cohesion is ensured by A^{2+} and A^{3+} cations. These layers exhibit a diamond-shaped perovskite configuration, with distorted MO_6 octahedra. The different members of the series (Fig 14) differ from

each other by the number n of octahedra which determines the thickness of the perovskite layers, the smallest member which has been observed in oxides being $\text{Ca}_2\text{Nb}_2\text{O}_7$ ($n = 4$). Non integral n values are also observed. they correspond to the stacking of layers of different thickness in the same oxide; these latter oxides are considered as intergrowths of two or several integral- n members. Such intergrowths may be ordered, or disordered, formed of two or more different n -members leading to giant cells which have been observed by electron microscopy.

The Aurivillius phases $\text{Bi}_2\text{O}_2\text{A}_{n-1}\text{M}_n\text{O}_{3n+1}$ ^(2-3,5,68-77)

The Aurivillius phases, which have been extensively studied for their ferroelectric properties form a very numerous family which can be formulated $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{n-1}\text{M}_n\text{O}_{3n+1})^{2-}$ with $A = \text{Ca}, \text{Sr}, \text{Ba}, \text{Pb}, \text{K}, \text{Na}, \text{Bi}$ and $M = \text{Ta}, \text{Nb}, \text{Ti}, \text{W}$.

This structural family is represented on Fig. 15 by the three first members, the koechlinite Bi_2MoO_6 ($n = 1$) studied for its catalytic properties and the ferroelectric oxides $\text{Bi}_2\text{SrNb}_2\text{O}_9$ ($n = 2$) and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ($n = 3$).

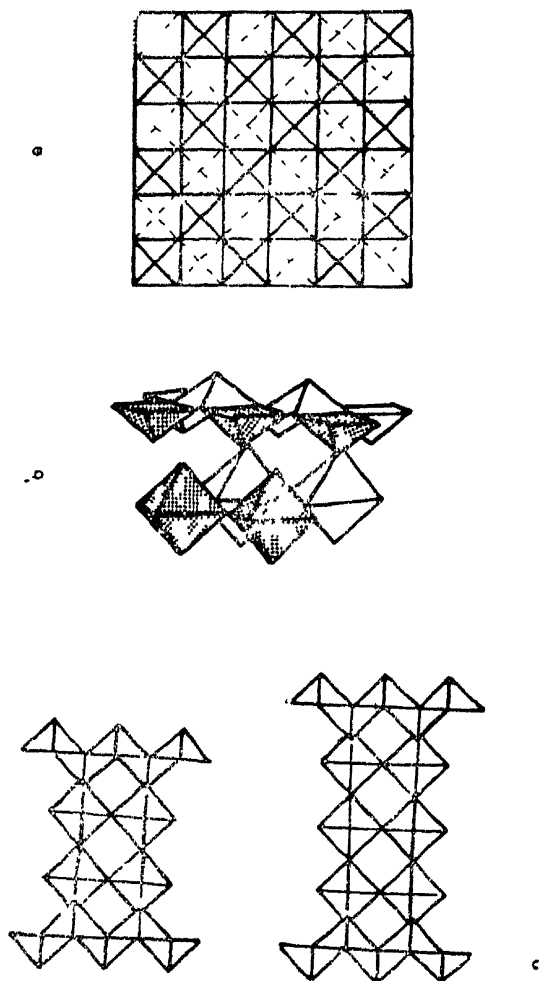


FIG 15 The Aurivillius phases The $(\text{Bi}_2\text{O}_2)^{2+}$ layer (a) koechlinite, $n = 1$ (b) schematic representation of $\text{Bi}_2\text{SrNb}_2\text{O}_9$, $n = 2$ (c) and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, $n = 3$ (d)

The structure of the different integral m members is formed of pyramidal (Bi₂O₂)²⁺ layers (Fig 15a) built up of edge-sharing BiO₄ pyramids alternately with multiple perovskite layers (Fig 15b, c, d) which are n octahedra thick. This class of oxides is very similar to the (AO)(AMoO₃) _{n} intergrowths : the (Bi₂O₂)²⁺ layers replace the sodium-chloride AO slabs whereas the perovskite slabs remain untouched. Nevertheless the AO(AMoO₃) _{n} oxides form a continuous three dimensional material and cannot be considered as a layer-structure contrary to the Aurivillius phases which consist of cationic and anionic infinite layers. The non-stoichiometry possibilities in these oxides are similar to those described for (AO)(AMoO₃) _{n} , as well as for A _{n} M _{n} O_{3 n +2} : for non integral n values and high n values ordered and disordered intergrowths of integral members are observed.

The structure of MoO₃⁽⁷⁸⁾

The structure of MoO₃ formed of neutral layers of edge-sharing distorted octahedra, whose cohesion is ensured by van der Waals forces can be deduced from the ReO₃-type framework in a very simple way, as shown formally on Fig. 16. The cooperative migration of one plane of MoO chains out of two in the MO₃-perovskite framework, i.e. the 001 shearing of one octahedral layer out of two (Fig 16a) leads to double edge sharing MO₃-perovskite layers already observed in {001} M _{n} O_{3 n -1} shear structures (Fig. 16b). The translation of one layer out of two along the direction perpendicular to the plane of the projection of half a height of an octahedron combined with a simple translation in this plane in order to bring them closer together leads to the MoO₃ layer structure (Fig. 16c). Thus, it appears that the MoO₃ structure can be considered as the consequence of a shearing mechanism in the ReO₃-type lattice

ADAPTABILITY OF THE ReO₃-TYPE FRAMEWORK AND TETRAHEDRA

The ability of the ReO₃-type framework to adapt PO₄ tetrahedra has been discovered recently with the very numerous family of the phosphate tungsten bronzes⁷⁹⁻⁹⁰. These oxides are generated by the replacement of one or two octahedra by a PO₄ tetrahedron or a diphosphate group in a "W₄O₂₀" unit (Fig 17). The O-O distance in the PO₄ tetrahedra, very close to those observed in the WO₆ octahedra, allows a junction without changing the angles of 90° which characterize the perovskite cages (Fig 17a). In the same way the height of the P₂O₇ group, close to that of a WO₆ octahedron, allows a connection without tilting drastically or disordering the WO₆ octahedra (Fig. 17b). As a result four main families of phosphate tungsten bronzes closely related to the perovskite have been isolated : the diphosphate tungsten bronzes with hexagonal tunnels (DPTB_H), the monophosphate bronzes with pentagonal tunnels (MPTB_P), and the diphosphate tungsten bronzes with pentagonal tunnels (DPTB_P), all characterized by metallic or semi-conductive properties.

The DPTB_H's A _{x} (P₂O₄)₂(WO₃)_{2 m} (A = K, Rb, Tl, Ba, $0 < x \leq 1$ and m = integral) have their host-lattice (P₂O₄)₂(WO₃)_{2 m} formed of ReO₃-type slabs connected through planes of diphosphate groups (Fig 18). The "perovskite" slabs are almost regular and their perovskite tunnels are empty. At the junction between two

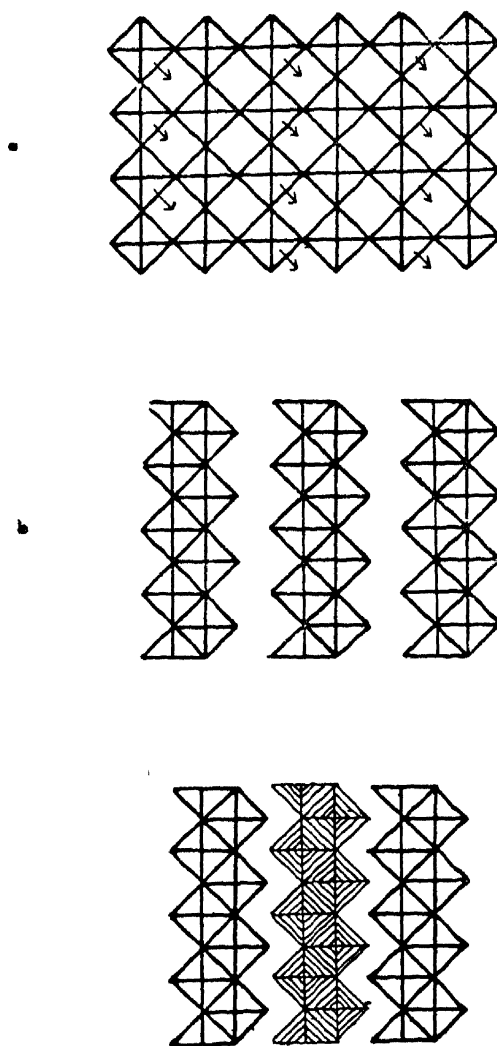


FIG 16 Cooperative migration of the MO chains in the ReO_3 -type structure (a) leading to $\{001\}$ CSP's (b) and finally to the MoO_3 structure

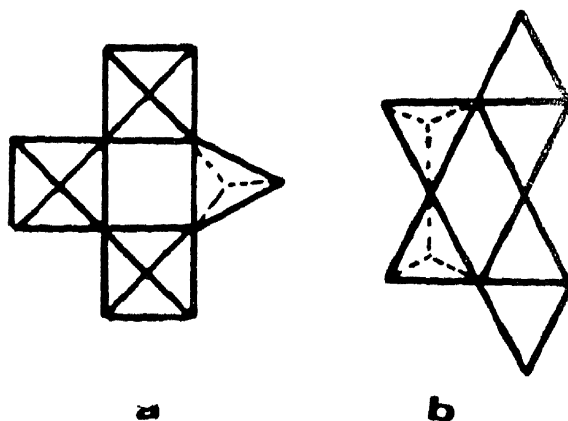


FIG 17 The adaptability of a tetrahedron (a) and of a P_2O_7 group (b) to the WO_6 octahedra. consecutive slabs the corner-sharing WO_6 octahedra and P_2O_7 groups form hexagonal tunnels where the A ions are located. The ReO_3 -type slabs have a variable

width characterized by the number m of corner sharing octahedra in the $[100]_P$ direction. Moreover, the even- m members (Fig. 18a) differ from the odd- m members (Fig. 18b) by a translation of one phosphate plane out of two. As a consequence, the perovskite slabs are all built up of identical chains of $m/2$ octahedra in the $[010]_P$ direction of the even- m members (Fig. 18a), whereas in the odd- m members, the octahedra chains parallel to $[010]_P$ of one slab are alternately formed of $\frac{m+1}{2}$ and $\frac{m-1}{2}$ octahedra (Fig. 18b). The tendency to form regular tunnels is remarkable: the hexagonal tunnels exhibit angles of 90° and 120°, while the perovskite tunnels are characterized by angles very close to 90°, and 60–120° are observed for the small diamond-shaped tunnels built up from two octahedra associated to two tetrahedra.

The MPTB_P's $(PO_2)_4(WO_3)_{2m}$ are also built up from ReO₃-type slabs connected through phosphate planes (Fig. 19) but in these oxides each PO₄ tetrahedron shares its four corners with WO₆ octahedra. At the junction between two perovskite slabs the WO₆ octahedra and PO₄ tetrahedra form pentagonal tunnels which are empty. Like the DPTB_H's, the different members of this series differ from each other by the width of the ReO₃-type slabs i.e. by the number m of octahedra in the $[001]_P$ direction and by the parity of m . In the even- m members (Fig. 19a) the perovskite slabs exhibit a constant width along $[110]_P$, whereas in the odd- m members (Fig. 19b) one phosphate plane out of two has been translated so that chains $\frac{m+1}{2}$ and $\frac{m-1}{2}$ octahedra alternate parallel to the $[110]_P$ direction. Moreover, in this series, the member $m = 5$, exhibits a second form whose host-lattice (Fig. 19c) is formed

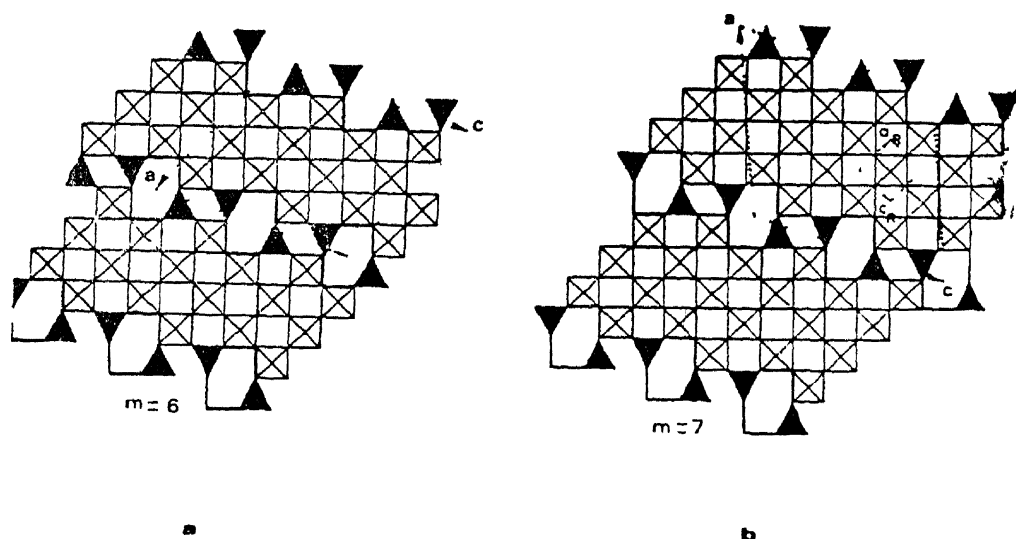


FIG 18 The structure of DPTB_H's $(P_2O_4)_4(WO_3)_{2m}$ (a) an even- m member $m = 6$ (b) an odd- m member $m = 7$.

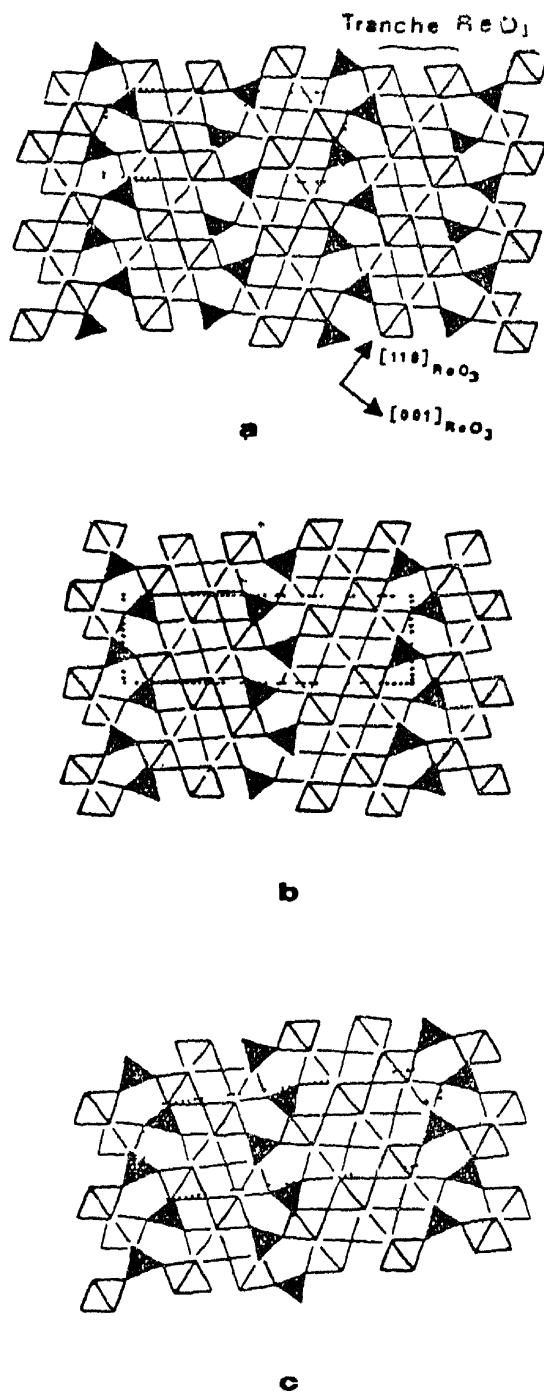


FIG 19 Structure of the MPTB_P's $(\text{PO}_2)(\text{WO}_3)_{2m}$ an even m member $m = 4$ (a), an odd- m member $m = 5$ (b), the second form of observed for $m = 5$ corresponding to the intergrowth of $m = 4$ and $m = 6$ (c)

of two different ReO_3 -type slabs which are six and four octahedra wide respectively, so that such a structure can be considered as an intergrowth of the two even members, $m = 4$ and $m = 6$

The third family, the MPTB_H's $A_x(\text{PO}_2)_4(\text{WO}_3)_{2m}$, is observed for $A = \text{Na}, \text{K}$ and an insertion rate greater than that of the DPTB_H's $1 < x \lesssim 2$. The structure

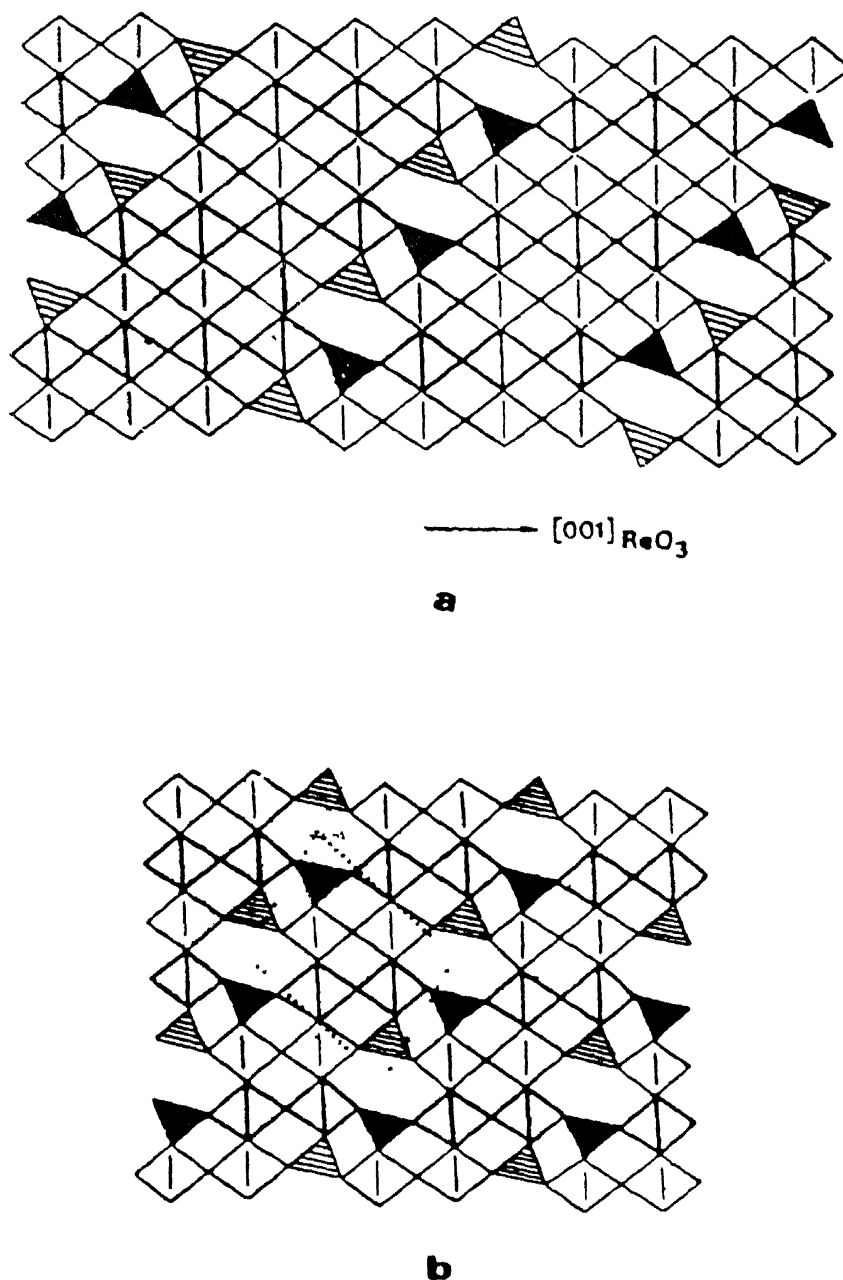


FIG 20 Structure of the MPTB_H 's $\text{K}_x(\text{PO}_3)_4(\text{WO}_3)_{2m}$ an odd- m member $m = 7$ (a) an even- m member $m = 4$

of these bronzes is composed of ReO_3 -type slabs identical to those of the MPTB_F 's and connected through "monophosphate planes" (Fig 20). These differ from the MPTB_F 's by their junction between two ReO_3 -type slabs in which the PO_4 tetrahedra and WO_6 octahedra form hexagonal tunnels where the A ions are located. In these oxides the odd- m members (Fig 20a) differ from the even- m members (Fig. 20b) by a translation of one phosphate plane out of two as shown for the potassium bronze $m = 4$ (Fig 20b). It is worthy of note that both frameworks MPTB_F 's and MPTB_H 's are very closely related they are both built up of quite identical MO_3 slabs

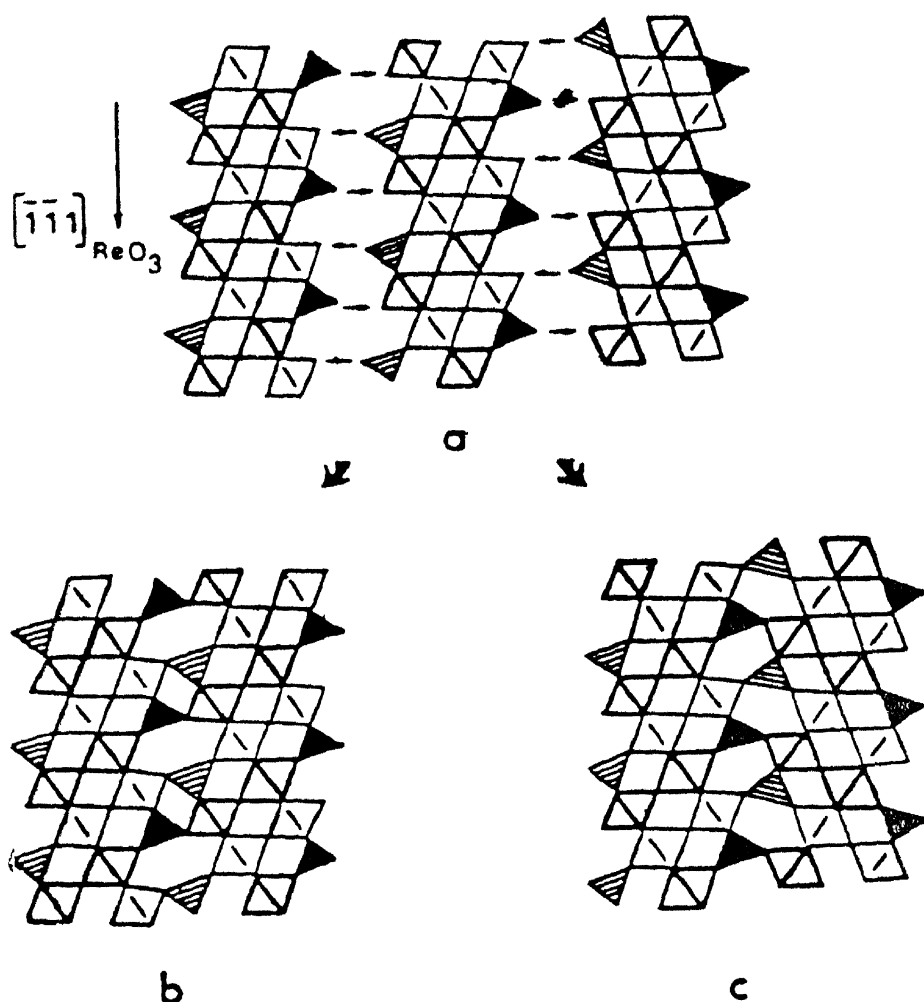


FIG 21 The identical MO_3 -slabs bordered with PO_4 tetrahedra (a) common to the $MPTB_H$'s (b) and to the $MPTB_F$'s (c)

bordered by PO_4 tetrahedra (Fig 21a) and differ only one from each other by the relative positions of the slabs. One passes from the $MPTB_H$'s structure (Fig 21b) to the $MPTB_F$'s structure (Fig 21c) by rotation of 180° of one slab out of two.

Besides these three classes of oxides which were synthesized in quantitative manner for a wide field of composition (m ranging from 4 to 16), the $DPTB_F$'s could be observed by HREM on microcrystals but could not be synthesized as pure compounds in the form of polycrystalline samples. The host-lattice of these bronzes (Fig. 22) is closely related to the one of $DPTB_H$'s in that one observes again MO_3 -perovskite slabs connected through diphosphate planes. But, contrary to the $DPTB_H$'s, the association of two P_2O_7 groups and two WO_6 octahedra at the junction of two perovskite slabs delimits pentagonal tunnels which seem to be unoccupied. Moreover, only a semiregular spacing of the diphosphate planes could be observed for those oxides.

It must be pointed out that all these bronzes exhibit single and multiple intergrowths for non-integral m -values, and for very high integral m -values.

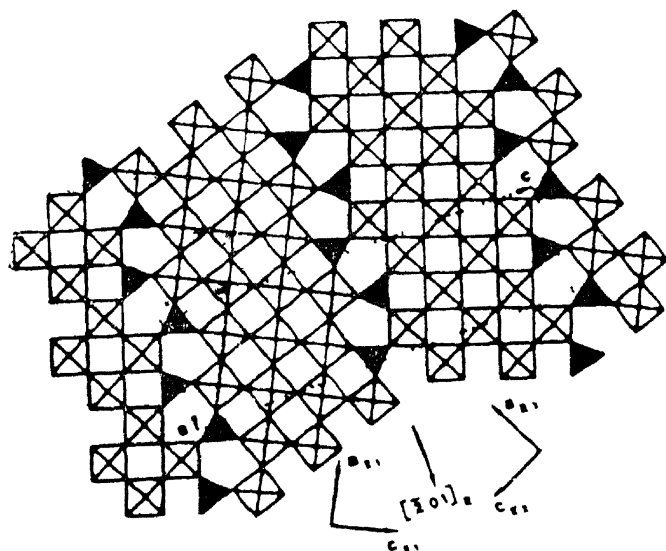


FIG 22 Idealized structure of the DPTB_p's the member $m = 7 (\text{P}_2\text{O}_4)(\text{WO}_3)_{2m}$.

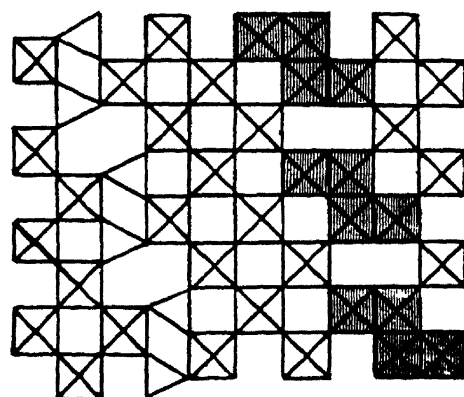


FIG 23 Transversal intergrowth of {102} CSP's and diphosphates planes

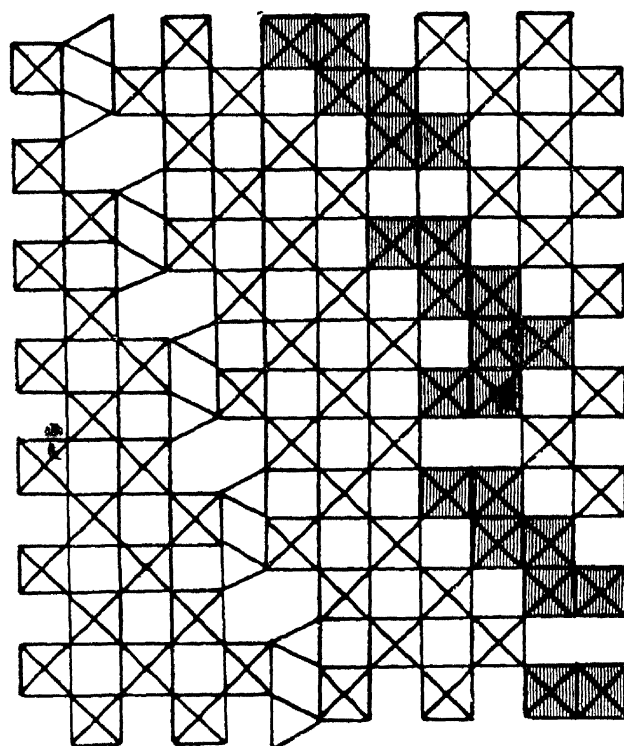


FIG 24 Transversal intergrowth of {001}—{103} CSP's and diphosphates planes.

These intergrowths which correspond to a sequence of different ReO_3 -type slabs may be either ordered or disordered according to the method of synthesis and the nominal composition of the samples. Many extended defects have been observed in these oxides by HREM which show the great flexibility of the perovskite framework.

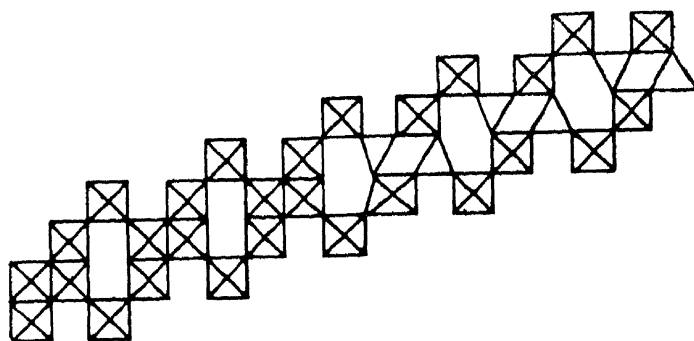


FIG 25 Longitudinal intergrowth of $\{102\}$ CSP's and diphosphates planes.

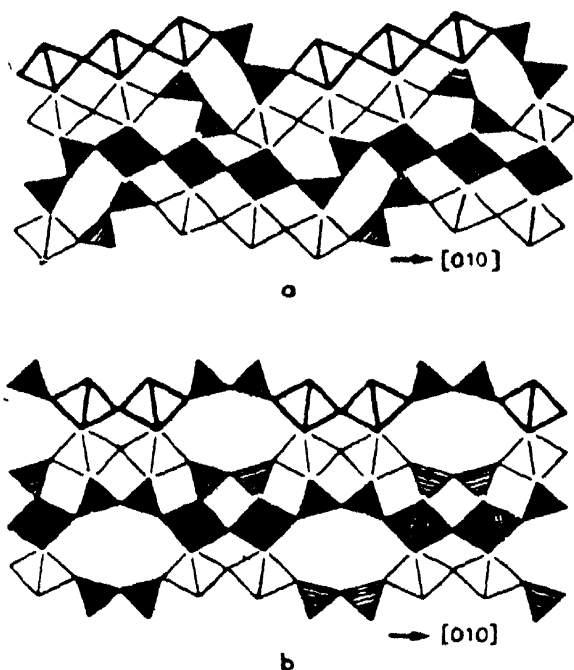


FIG 26 Structure of $P_8W_{12}O_{52}$ (a) and $CsP_8W_8O_{40}$ (b)

It is not possible to present here all these studies. Nevertheless one can mention as examples the possibility of formation of regular transversal intergrowths of $\{102\}$ CSP and diphosphates planes in a MO_3 matrix (Fig 23), or transversal intergrowths of complex $\{001\}$ — $\{103\}$ CSP and diphosphate planes (Fig 24) or longitudinal intergrowths of $\{102\}$ CSP and diphosphate planes (Fig 25).

Besides these bidimensional conductors, other phosphorus tungsten oxides such as $P_8W_{12}O_{52}$ ⁽⁹¹⁾ and $CsP_8W_8O_{40}$ ⁽⁹²⁾ emphasize the great adaptability of the PO_4 tetrahedra to the MO_3 -perovskite framework. The first one has its framework (Fig 26a) formed of perovskite columns built up of 2×3 octahedra which are linked together sometimes through the vertices of their octahedra, sometimes through diphosphate groups, this framework forms pentagonal, "hexagonal" and perovskite tunnels which are empty. The bronze $CsP_8W_8O_{40}$ whose host lattice (Fig 26b) is formed of corner-sharing WO_6 octahedra and diphosphate groups is remarkable

by its octagonal tunnels where the Cs⁺ ions are located. In spite of this particularity this structure is very closely related to the perovskite in that one observes "M₄O₂₀" units which form perovskite columns perpendicular to the plane of the projection. These columns are completely isolated, i.e. they are only linked to P₂O₇ groups so that such a bronze should present a unidimensional conductivity.

The possibility to adapt tetrahedra to the MO₃-perovskite lattice is not limited to the phosphate tungsten bronzes. The oxides γ and η Mo₄O₁₁⁹³⁻⁹⁴ correspond to the members $m = 6$ of the MPTB_F's and the MPTB_H's respectively, while NbPO₅ and NbTaO₅⁹⁵ represent the second member of the MPTB_F's. In the same way the molybdenum bronzes $A_x\text{Mo}_6\text{O}_{17}$ ($A = \text{Na}, \text{K}, 0.8 < x \leq 1$) which exhibit a layer structure⁹⁶⁻⁹⁸ are related to the MPTB_F s. Their structure (Fig 27) is characterized by four octahedra-wide perovskite layers bordered by MO₄ tetrahedra, the cohesion between these layers is ensured by the A⁺ ions.

CREATION OF ANIONIC VACANCIES IN THE PEROVSKITE STRUCTURE

The ReO₃-framework, owing to its great flexibility, is at the origin of new structural families, which can be deduced from the perovskite structure by ordered formation of anionic vacancies. In order to form AMo_{3-x} perovskites, the M cation must be able to take besides the octahedral coordination smaller coordinations (tetrahedral, pyramidal, square planar, etc.). Such a situation can be realized by the presence on the M sites either of two different metallic elements or of mixed valence elements. In this respect elements such as iron, copper, manganese and cobalt are potential candidates owing to their ability to take several oxidation states and several coordinations.

*From Perovskite to β -Cristoballite via Brownmillerite Oxygen-Defect Perovskites built up from Octahedra and Tetrahedra*⁹⁹⁻¹¹⁴

Starting from the ReO₃-type framework (Fig. 28a), new mixed frameworks can be generated by creation of rows of oxygen vacancies parallel to [110]_P in an octa-

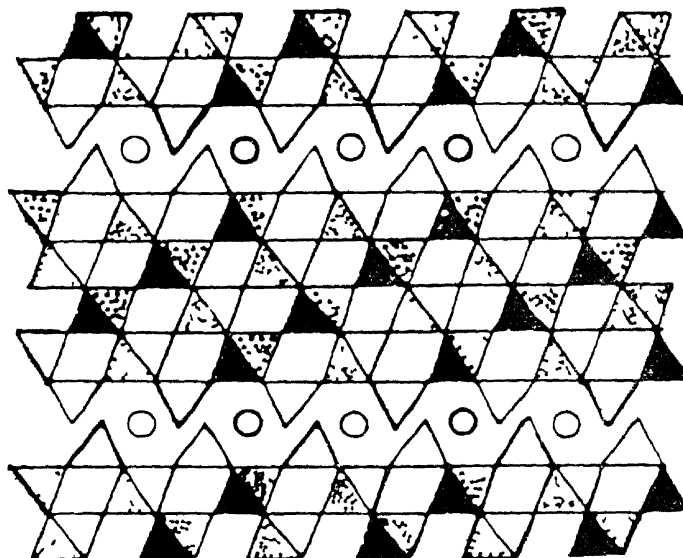


FIG 27 The structure of the molybdenum bronze AMo_6O_{17} ($A = \text{Na}, \text{K}$)

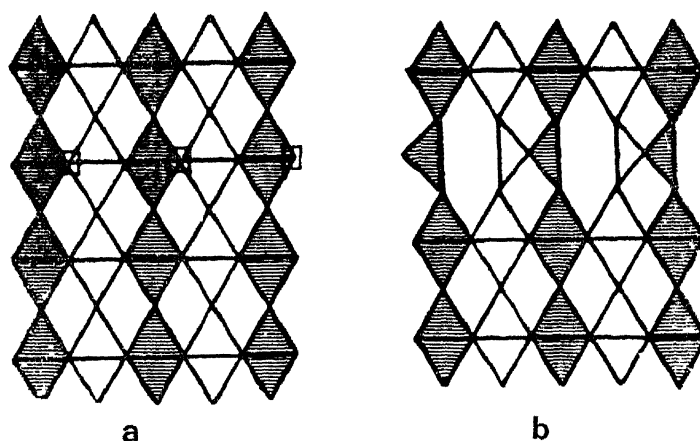


FIG 28 The creation of rows of oxygen vacancies in the MO_6 framework along $\langle 110 \rangle_P$ (a) leads to the formation of slabs of tetrahedra (b).

hedral slab in such way that one vacant row alternates with a fully occupied one leading to a tetrahedral slab (Fig 28b). This “mechanism” of formation of vacancies leads to the oxygen-deficient perovskites $(AMO_3)_n AMO_2$ □ whose host lattice is built up from multiple perovskite layers connected through planes of MO_4 tetrahedra as shown for the three first members of the series (Fig 29). The integral number n corresponds to the number of octahedra which determines the thickness of the perovskite slabs. Numerous phases corresponding to different n values have been isolated in the systems $Ca_2Fe_2O_5-ATiO_3$ ($A = Ba, Sr, Ca$) and $Ca_2Fe_2O_5-AFeO_3$ ($A = Y, La, Gd$), in which iron exhibits simultaneously two coordinations, tetrahedral and octahedral, and one oxidation state $+3$, and in the system $SrFeO_3-Sr_2Fe_2O_5$, where iron exhibits a mixed valence $Fe^{3+}-Fe^{4+}$. In all these oxides many intergrowths of two integral n -members have been observed for non integral m values as shown for instance for $Ca_5Fe_5O_{13}$ ($n = 1.5$) which corresponds to the intergrowth of the members $m = 1$ and 2 (Fig 29d). More complex ordered and disordered intergrowths are frequently observed in these systems in which iron can be partially replaced by manganese.

The brownmillerite structure $Ca_2Fe_2O_5$, also observed for Ca_2FeAlO_5 , Ca_2FeCoO_5 and $Sr_2Co_2O_5$, first member of this series (Fig 29a) differs from the other members of the series in that one layer of tetrahedra out of two is translated, it results a doubling of the b parameter with respect to the hypothetical structure (Fig 30a) which would correspond to the same composition. If one carries on the process of ordered creation of rows of anionic vacancies parallel to $[110]_P$ in this latter structure (Fig. 30a), a tetrahedral framework is obtained (Fig 30b) which is in fact the one of β -cristoballite.

Oxygen-Defect Perovskites and Related Structures built up from MO_6 Octahedra and MO_5 Pyramids¹¹⁵⁻¹²⁵

The creation of rows of oxygen vacancies parallel to the $[001]$ direction of the cubic perovskite cell leads to the formation of a series of oxides whose framework is built up of MO_5 pyramids and MO_6 octahedra. The resulting framework forms

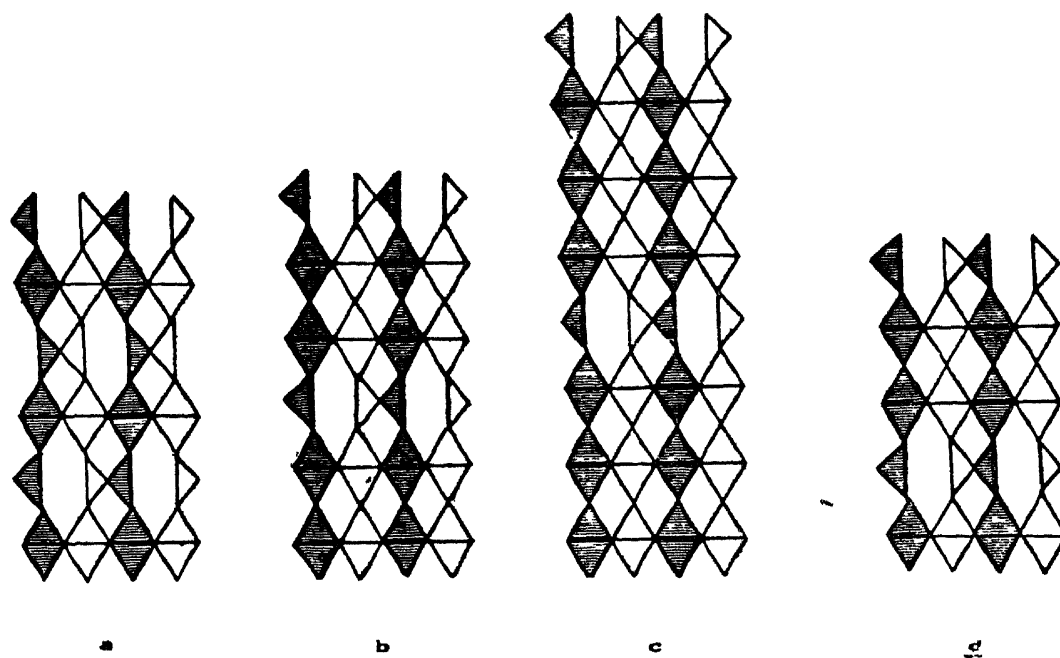


FIG 29 The oxygen defect perovskites $(\text{AMO}_3)_n\text{AMO}_2$ (a)—Brownmillerite $n = 1$, (b) $n = 2$, (c) $n = 3$, (d) $n = 1.5$ intergrowth of $n = 1$ and $n = 2$

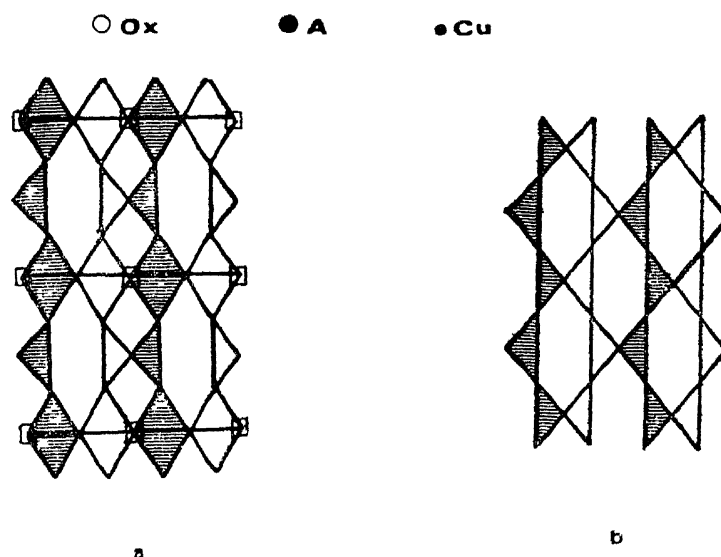


FIG 30 Ordered creation of anionic vacancies in the hypothetical second form of $\text{A}_2\text{M}_2\text{O}_5$ first member of the series $(\text{AMO}_3)_n\text{AMO}_2$ leading to the β -cristoballite ($n = 0$) (b)

hexagonal tunnels where the A ions are located. Copper, cobalt and especially manganese oxides are characterized by their ability to form such oxygen defect perovskites. For instance the anion deficient system CaMnO_{3-x} exhibits at least twelve different ordered oxygen-deficient perovskite structures: four different forms for the limit composition $\text{CaMnO}_{2.5}$, and four forms for $\text{CaMnO}_{2.75}$, two forms for $\text{CaMnO}_{2.667}$, and one form for $\text{CaMnO}_{2.556}$ and $\text{CaMnO}_{2.8}$. $\text{Sr}_2\text{Mn}_2\text{O}_5$, $\text{Ca}_2\text{Co}_2\text{O}_5$ and $\text{BaLa}_4\text{Cu}_5\text{O}_{13}$ belong to this class of compounds.

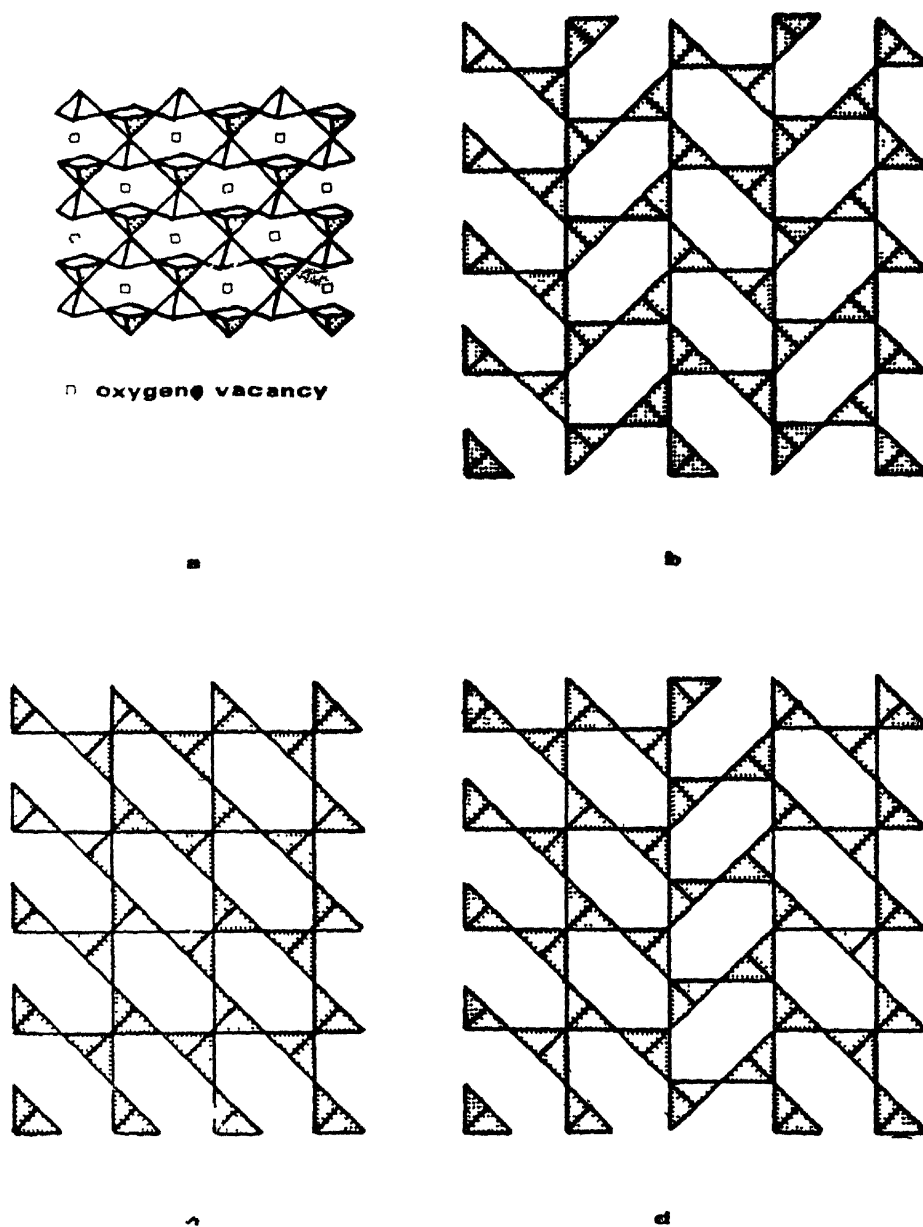


FIG 31 Structure of $\text{Ca}_2\text{Mn}_2\text{O}_5$ —schematic drawings corresponding to the major form (*a* & *b*) showing the rows of oxygen vacancies parallel to $[001]_P$ in the ReO_3 -type framework (*a*) and the MnO_5 pyramids forming rows of hexagonal tunnels (*b*) and schematic structures of two other minor forms (*c*-*d*) showing different orientations of the rows of tunnels

A complete discussion of all these oxygen deficient perovskites is not possible here. Nevertheless it can be stated that all these frameworks result from the ordered elimination of rows of oxygen atoms parallel to $[001]_P$ in the ReO_3 -type framework. The different forms of $\text{Ca}_2\text{Mn}_2\text{O}_5$ are all characterized by corner-sharing MnO_5 pyramids in agreement with the unique presence of the Jahn-Teller ion Mn(III) ; these forms differ only from each other by the relative orientation of the rows of hexagonal tunnels. It is easy to understand from the comparison of the structure of the most currently observed phase (Fig 31*a, b*) for $\text{Ca}_2\text{Mn}_2\text{O}_5$ with

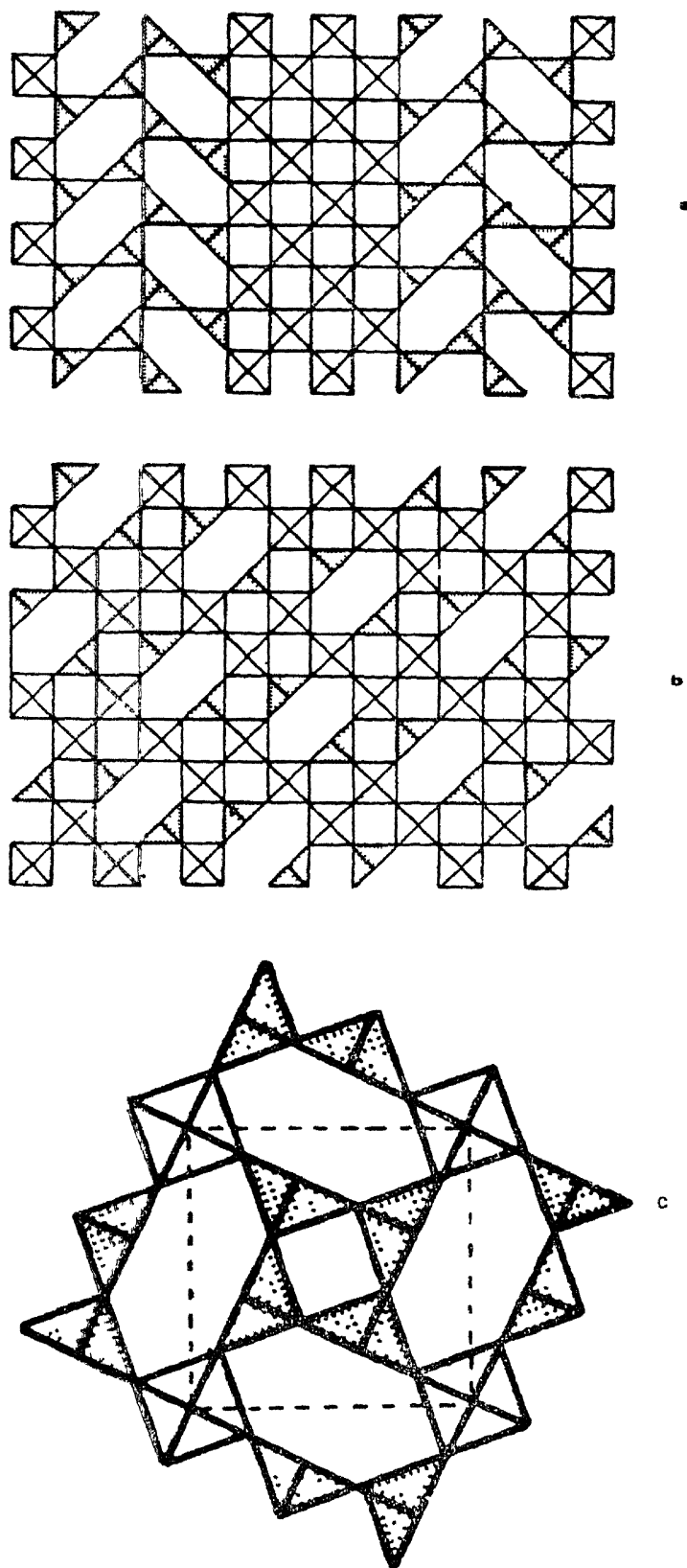


FIG 32 Some examples of ordered oxygen defect perovskites built up from corner-sharing MO_6 pyramids and MO_6 octahedra (a) - one form of $\text{CaMnO}_{2.75}$ (b) $\text{Ca}_2\text{MnO}_{2.80}$ (c) $\text{BaLa}_4\text{Cu}_5\text{O}_{13}$

two other forms (Fig. 31c, d), observed in minor amounts, that many polytypes can be predicted, these phases consist of identical rows of hexagonal tunnels parallel to $[110]_P$ and differ from each other only by the relative orientation of the successive tunnel rows. The ordered insertion of oxygen in the hexagonal tunnels of the different $\text{Ca}_2\text{Mn}_2\text{O}_5$ forms may lead to mixed valence oxygen deficient perovskites built up from multiple rows of hexagonal tunnels, i.e. multiple slabs of MnO_5 pyramids parallel to $(110)_P$ which alternate with multiple ReO_3 -type slabs as shown for instance for one form of $\text{CaMnO}_{2.75}$ (Fig. 32a) which is obtained by insertion of oxygen in the $\text{Ca}_2\text{Mn}_2\text{O}_5$ form described in Fig. 30b. Many other complex organisations of these hexagonal tunnels, resulting from mixed frameworks built up from octahedra and tetrahedra have been observed for intermediate compositions between $A_2M_2O_5$ and the stoichiometric perovskite as shown for instance for $\text{Ca}_2\text{MnO}_{2.8}$ (Fig. 32b) and the metallic conductor $\text{BaLa}_4\text{Cu}_5\text{O}_{13}$ (Fig. 32c).

The possibility of formation of mixed layers built up from MO_5 pyramids and MO_6 octahedra can be extended to the intergrowths $\text{AO}(\text{AMO}_3)_n$. The oxides $\text{La}_{2-x}\text{A}_{1+x}\text{CuO}_{6-x/2+\delta}$ ($A = \text{Ca}, \text{Sr}$) are one example of such a possibility the structure of the limit compound $\text{La}_2\text{SrCu}_2\text{O}_6$ (Fig. 33a) corresponds to the second member of the intergrowth in which the AO layer remains stoichiometric whereas the double perovskite layer is oxygen-deficient in such a way that it is only formed of corner-sharing CuO_5 pyramids. It is worthy of note that such a Cu(II) -oxide can intercalate oxygen in a reversible manner, leading to the mixed-valence oxides $\text{La}_2\text{SrCu}_2\text{O}_{6+\delta}$ in which the oxygen-deficient perovskite slabs are built up from CuO_6 octahedra and CuO_5 pyramids. The oxides $\text{La}_{2-x}\text{A}_x\text{Cu}_{4-x/2+\delta}$ ($A = \text{Cu}, \text{Sr}$) are closely related to the oxides $\text{La}_{2-x}\text{A}_{1+x}\text{Cu}_2\text{O}_{6-x/2+\delta}$ they represent the first member of the intergrowth (Fig. 33b) formed of AO stoichiometric layers and single oxygen deficient perovskite layers. Moreover they differ from the second member, in that the oxygen vacancies are located in the basal plane of the CuO_6 octahedra. The mixed valence character of copper in these oxides, and their ability to intercalate oxygen make that they exhibit a p -type conductivity ranging from a semi-conductive to a metallic character.

*Oxygen-Defect Perovskites and Related Structures involving Copper in Square Planar Coordination*¹²⁶⁻¹³²

The ability of copper to take two oxidation states Cu II-Cu III and several coordinations—octahedral, pyramidal, square planar—makes that mixed valence oxygen-deficient perovskites or related structures can be isolated for copper oxides, in which copper exhibits the square planar coordination. The oxygen defect perovskite $\text{La}_3\text{Ba}_3\text{Cu}_6\text{O}_{14+\delta}$ and the isostructural oxides $\text{Ba}_3\text{La}_{3-x}\text{Ln}_x\text{Cu}_6\text{O}_{14+\delta}$ ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Yb}, \text{Er}, \text{Y}$), and the oxides ACuO_2 ($A = \text{Ca}, \text{Sr}$), A_2CuO_3 and CaCu_2O_3 derived from the perovskite are the main examples of this particular behaviour of copper.

The structure of the reduced form $\text{La}_3\text{Ba}_3\text{Cu}_6\text{O}_{14}$ (Fig. 34) can be deduced from the one of stoichiometric perovskite by creation of oxygen vacancies in the SrO -type

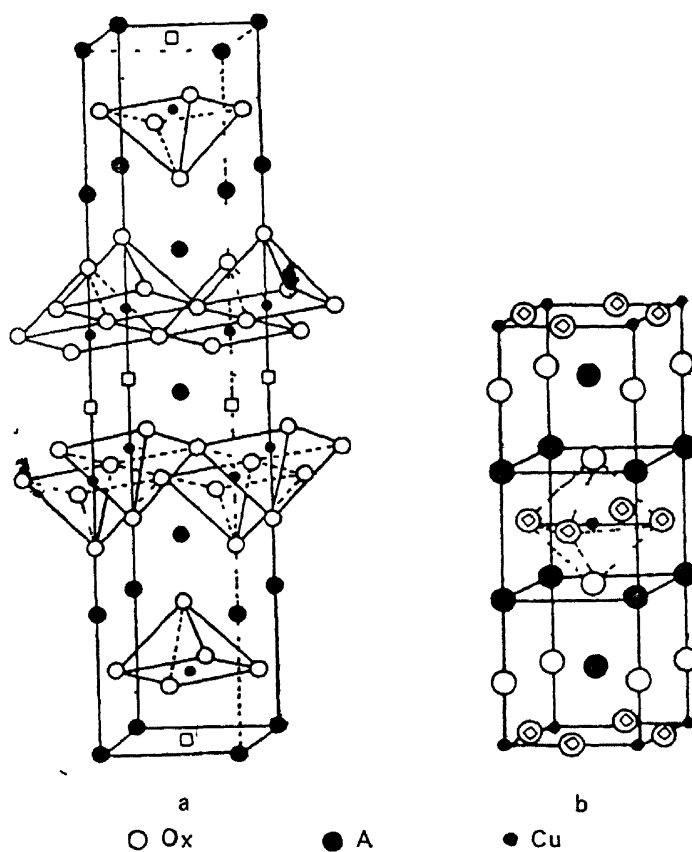


FIG 33 The oxygen deficient intergrowths $AO [AMO_{3-x}]_n$ (a) The oxide $La_2SrCu_2O_6$ ($n = 2$) and (b) the oxides $La_{2-x}A_xCu_{4-x/2+\delta}$ ($m = 1$)

planes in an ordered way. It results that the sequence $(AO-CuO_2)$ along a in the cubic perovskite is replaced by the sequence $Cu_2O_4-A_2O \square-A_2 \square_2-Cu_2O_4-A_2O \square$ in $La_3Ba_3Cu_6O_{14}$. In this structure, copper exhibits simultaneously three sorts of coordinations: octahedral, pyramidal and square planar. The remarkable feature of this structure concerns the great oxygen defect with respect to perovskite: more than 22 per cent of the anionic sites are unoccupied, in spite of the presence of a notable amount of Cu(III). This explains the intercalation properties of this oxide, which can intercalate oxygen, without changing its structure. The oxide $La_3Ba_3Cu_6O_{14+\delta}$, like the other mixed valence copper oxides described here, is a p -type conductor whose conductivity increases drastically as the amount of intercalated oxygen increases.

The structure of the oxides A_2CuO_3 (Fig 35a) can be generated from the first member of the intergrowth $AO(AMO_3)_n$, i.e. " A_2CuO_4 ", by elimination of one "plane" of oxygen atoms out of two in the perovskite slab, whereas the SrO-type slabs remain untouched (Fig 35b). This creation of oxygen vacancies leads to the formation of (CuO_2) planes built up from corner-sharing square planar CuO_4 groups. Moreover, the (CuO_2) planes are brought closer together, involving a contraction of the AO layers (the b parameter perpendicular to the plane of the projection changes from $3.9 \text{ \AA}$ to $3.5 \text{ \AA}$). It must be pointed out that, no intergrowth between Sr_2CuO_3

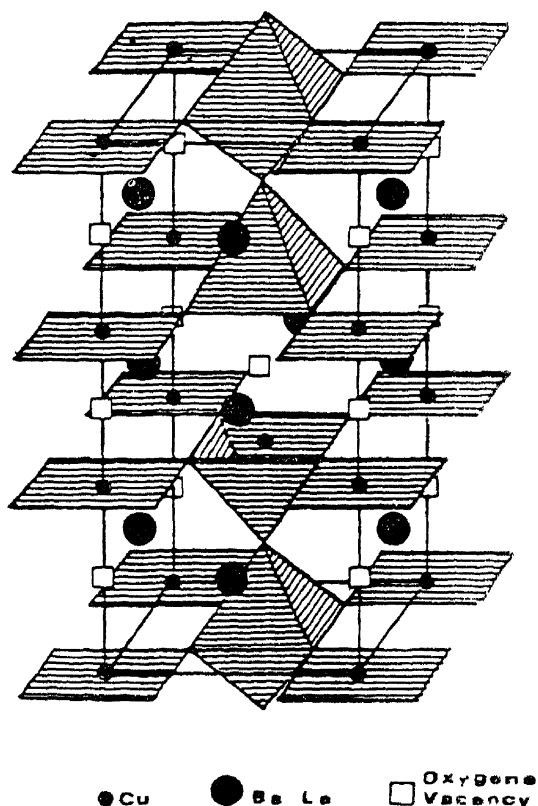


FIG 34 The oxygen deficient perovskite $\text{La}_3\text{Ba}_1\text{Cu}_6\text{O}_{14.8}$.

and A_2CuO_4 oxides has been observed in spite of the existence of a bidimensional accord along $(010)_{\text{K}_2\text{NiF}_4}$ between the two structures.

The structural filiation of the oxygen deficient perovskites can be carried on by comparing the structure of SrCuO_2 and $\text{SrCu}_{0.75}\text{Ni}_{0.25}\text{O}_2$ (Fig 36a) with that of Sr_2CuO_3 (Fig 35a). This structure consists also of SrO -type slabs and slabs of CuO_4 groups. It exhibits also a bidimensional accord with the Sr_2CuO_3 structure (see Fig 35a¹⁰⁰ plane) but it differs from it by the fact that the CuO_4 groups share their edges. The relationship between the two structures can be understood by considering that Sr_2CuO_3 is the first member of the hypothetical series $\text{AO}[\text{CuO}_4]_n$ obtained by creation of oxygen vacancies in the intergrowth $\text{AO}[\text{CuO}_3]_n$. The crystallographic shearing of the $(\text{CuO}_2)_2$ slab of the second hypothetical member $\text{SrO}[\text{CuO}_2]_2$ (Fig 36b) leads to the SrCuO_2 -type structure. Thus, SrCuO_2 can be described as a structure derived from the intergrowth of sodium chloride type- ReO_3 type $\text{AO}([\square]\text{MO}_3)_2$ by an ordered creation of rows of oxygen atoms in the ReO_3 -type slab followed by a crystallographic shear operation in this slab.

The oxide CaCu_2O_3 (Fig 37) exhibits also a similarity with Sr_2CuO_3 and SrCuO_2 as shown by the presence of layers of CuO_4 groups. However, it differs from the other two structures by the absence of SrO -type slabs. One observes Cu_2O_3 planes built up from distorted square planar groups CuO_4 , sharing sometimes their corners like in Sr_2CuO_3 , and sometimes their edges like in SrCuO_2 . In fact

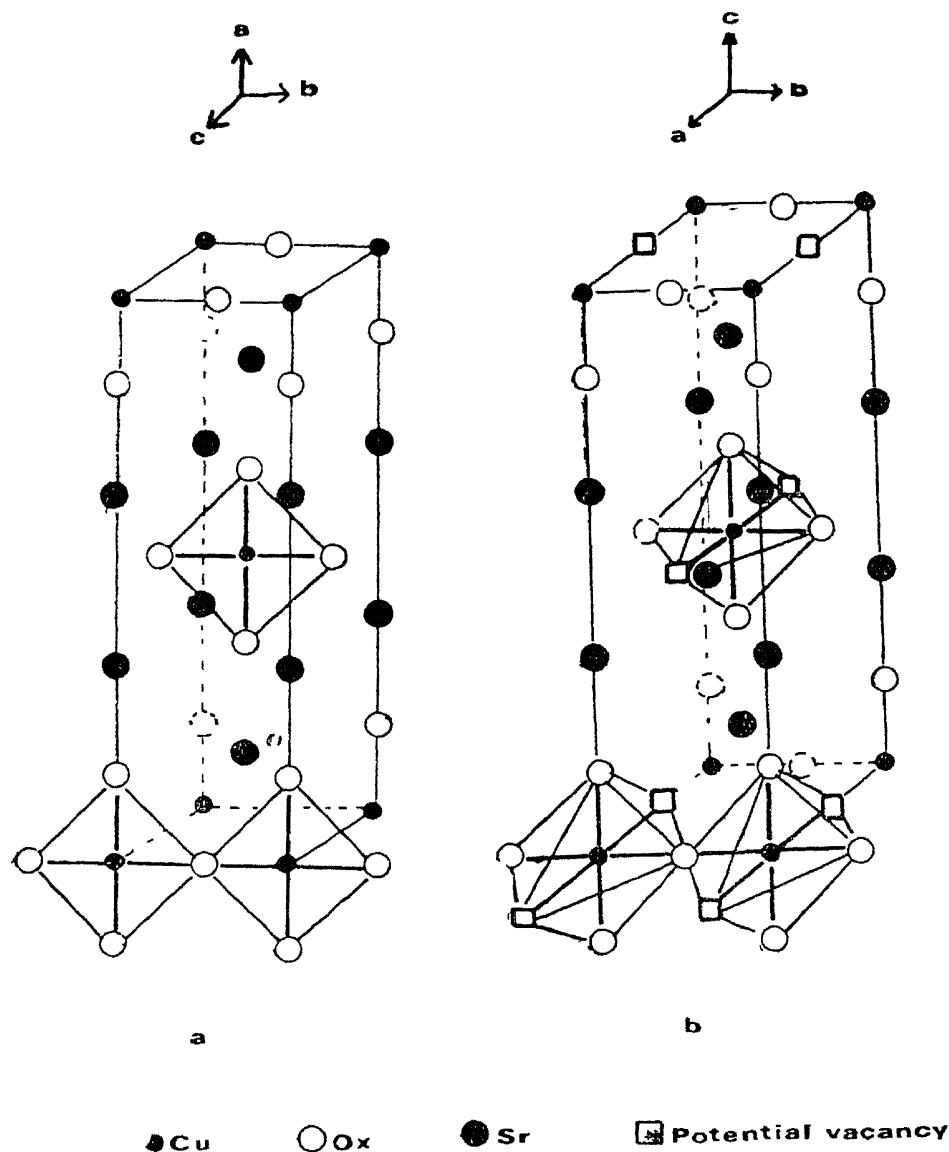


FIG 35 The structure of Sr_2CuO_3 (a) can be deduced from the K_2NiF_4 -type structure (b) by elimination of one "plane" of oxygen atoms out of two ($\square$) parallel to $(010)_{\text{K}_2\text{NiF}_4}$

this structure is closely related to the $\text{W}_n\text{O}_{3n-1}$ shear structures characterized by one sort of $\{001\}$ CSP. Its layers Cu_2O_3 can be deduced from the hypothetical member $m = 2$ (" W_2O_5 ") (Fig 38a) by suppression of the oxygen atoms located on both sides of the CuO_4 basal plane of the octahedra (Fig 38b), and then by bringing the Cu_2O_3 layers closer together. The calcium ions are inserted in the octahedral cavities formed by the CuO_4 groups.

Other Oxygen-Defect Perovskites^{3,133-135}

Other oxygen-defect perovskites have been isolated, whose structure is not completely determined to our knowledge besides oxides such as $\text{SrTiO}_{2.5}$ and $\text{SrVO}_{2.5}$, the oxides $\text{La}_n\text{Ni}_n\text{O}_{3n-1}$ seem to be very promising.

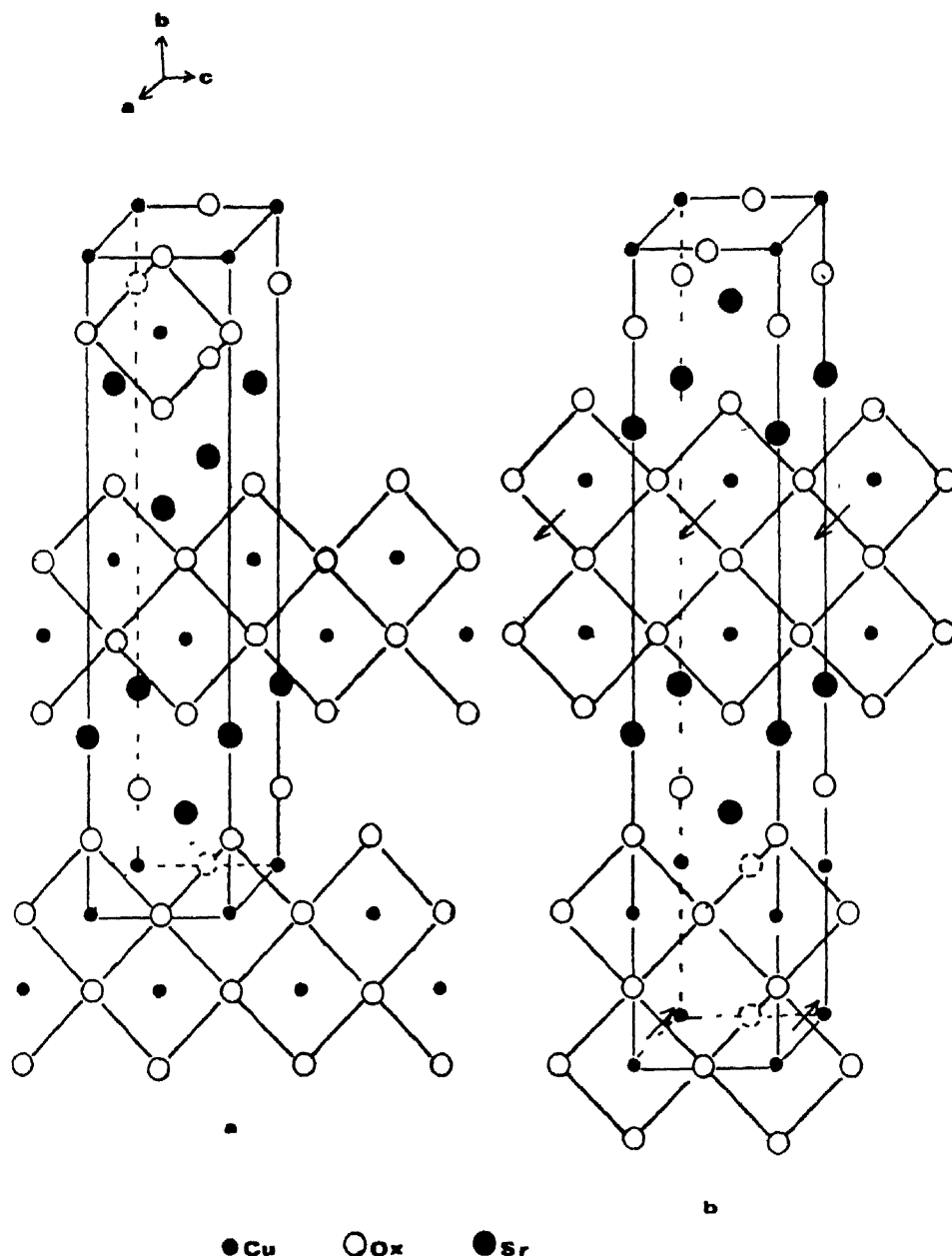
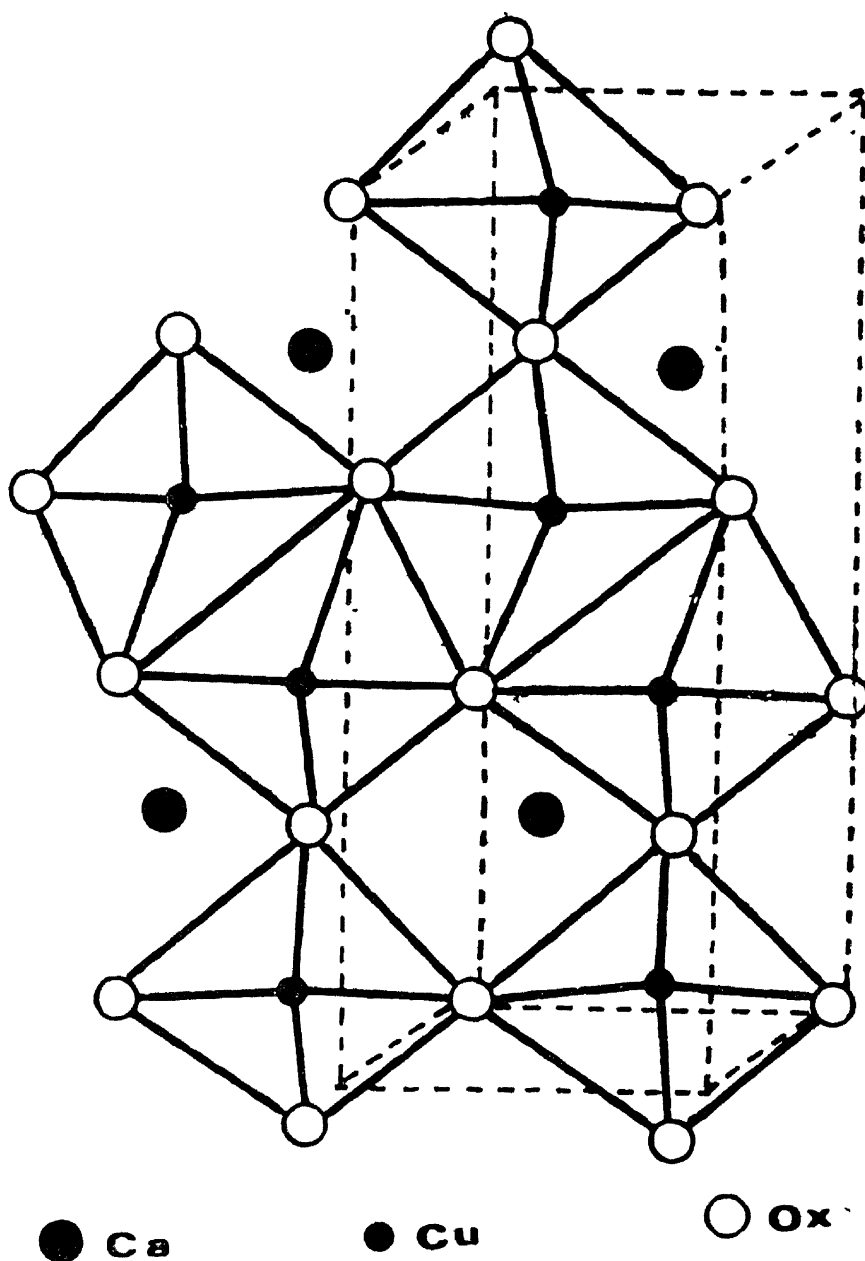
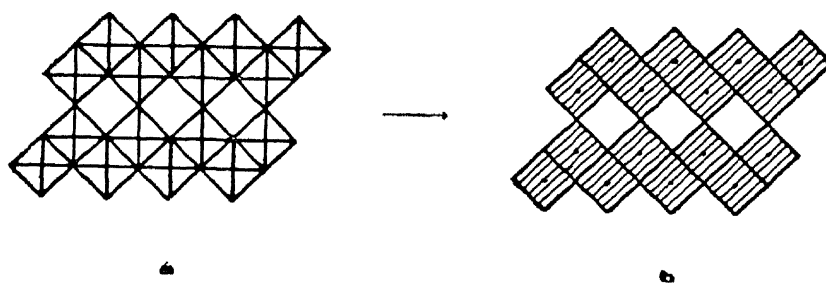


FIG 36 The structure of SrCuO_2 (a) and the hypothetical structure of the member $n = 2$ of the hypothetical series $\text{AO}(\text{CuO}_2)_n$. (b) The arrows correspond to the direction of the shearing

CONCLUSION

The ReO_3 -type structure can be considered as a very important precursor in the generation of new structural families. New structures can indeed be generated from this very simple and flexible framework in different manners: deformation of the framework by compression without major distortion of the octahedra, shearing phenomena, ordered formation of anionic vacancies, intergrowth resulting from a bidimensional accord with other structures, adaptability to other polyhedra and especially to tetrahedra. From this structural affiliation it appears that the ReO_3 -


FIG 37 The structure of CaCu_2O_3

FIG 38 The transformation of the “ W_2O_5 ” shear structure (a) into the “ Cu_2O_3 ” layers (b) by ordered elimination of oxygen atoms

type framework is closely related to the structure of different oxides such as the MO oxides with rock-salt structure, anatase and β -cristoballite

It is also clear that the octahedral " M_4O_{20} " limits can be considered as fundamental structural units which can participate to the edification of numerous structures of oxides. Perovskite columns built up from such " M_4O_{20} " units can indeed be recognized in many oxides which have not been described here, such as molybdenum and tungsten oxides with a tunnel structure, V_6O_{13} , Na_xTiO_3 bronzes, $BaTi_2O_5$ and so on.

It must finally be emphasized that another aspect of this structure has not been analyzed here: its relationship with the close-packed oxides. The consideration of the ReO_3 -type structure along the $\{111\}$ direction of the cubic cell and the insertion in the lattice of a A cation with the same size as that of oxygen ($A = Ba^{2+}$, K^+) leads to a description of the structure in terms of an ABC close-packing of AO_3 layers, which form octahedral sites where the M ions of the AMO_3 perovskite are located. Many cation deficient "perovskites" $AM_{1-x}O_3$ correspond to this description: they are characterized by a regular stacking of AO_3 layers and the M cations and vacancies exhibit generally an ordered distribution in the octahedral sites, involving often the presence of face-sharing octahedra, and a hexagonal symmetry of superstructures. In the same way several hexagonal perovskites such as $BaMO_{3-x}$ ($M = Mn, Fe, Co$) exhibit oxygen defects with for some of them an ordered distribution. All these "close-packed perovskites" are closely related to the different close-packings observed for other oxides. The study of the relationships between these different close-packed structures covers a wide field which cannot be developed here. Many oxides derived from the ReO_3 -type structure exhibit interesting electron transport, magnetic, or catalytic properties. Thus, it appears that the systematic investigation of different systems of oxides, in a predictive manner, should allow to isolate new materials with specific properties and to establish a correlation between the structure and their properties.

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PROBLEMS OF SOLID STATE CHEMISTRY UNDER HIGH PRESSURE CONDITIONS : A PERSPECTIVE FOR ELABORATING NEW MATERIALS*

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Use of high pressures for preparing either classical materials with a high reaction speed or novel materials is illustrated by appropriate examples involving in particular high oxidation states. The technique has also been applied to crystal growth or to phase transformations favoured by lattice shrinking. The importance of high pressure as a physical parameter in modern solid state chemistry is emphasized.

Key Words : Solid State Chemistry; Synthesis; Structural Transformations; High Pressure; High Oxidation States

INTRODUCTION

THE high pressure technique is quite an efficient tool for preparing new materials of weak stability or of metastable character in solid state chemistry.

During the last few years it has led to a growing number of contributions, especially in three areas :—

- Synthesis of new materials either for better basic approach of scientific problems or for industrial applications
- Structural transformations
- *In situ* evolution of some physical properties under increasing pressure.

SYNTHESIS OF NEW MATERIALS

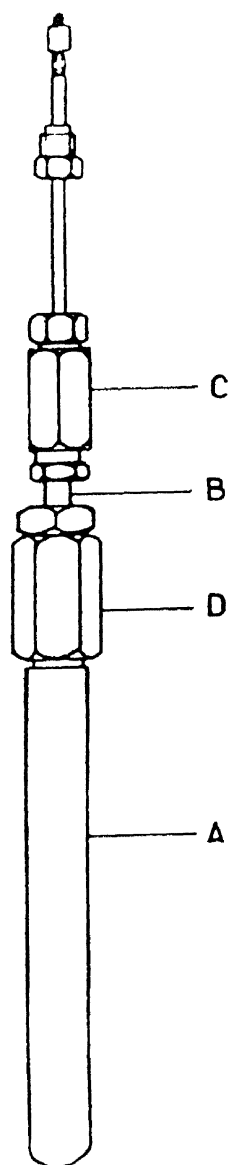
The performances have developed much thanks to utilization of equipments allowing higher pressures with better reliability and more safety. Figs. 1 and 2 give examples of apparatus used either for solid-gas reactions or for solid state synthesis.

The most important features in high pressure synthesis are either of kinetical nature or a stabilizing effect.

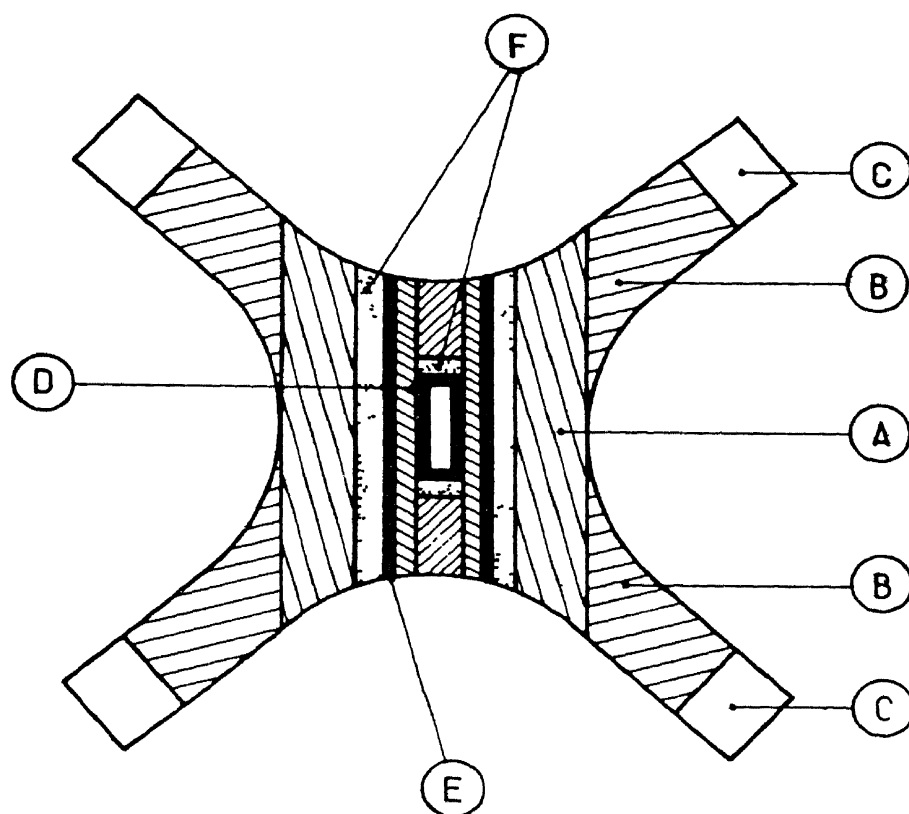
Kinetical Aspect

The reactions in high pressure conditions are considerably accelerated as far the expected material becomes thermodynamically more stable under pressure.

Such a behaviour is clearly illustrated by the synthesis of the distorted perovskite GdFeO_3 at atmospheric pressure at about 1000 °C, 50 hours are necessary to prepare a pure perovskite phase from the stoichiometric mixture of the starting



← FIG 1 Cold gasket gas reaction tube—A : reaction cylinder in refractory alloy, B : closing path, C : high pressure gasket, D : air proof crown.



↑ FIG 2 Belt-type apparatus used for reactions in sealed tubes (in solid state or of gas-solid type)

binary oxides. At the same temperature under 50kb pressure a much shorter time—between 8 and 10 minutes—is sufficient for realizing the same synthesis process ¹

High Pressure and Thermal Decomposition

High pressures are also extremely suitable to prevent unstable starting oxides from thermal decomposition, when the reaction requires normally high temperatures. This stabilization effect can be illustrated by the synthesis of the mercury tungsten bronzes Hg_xWO_3 . In spite of the thermal instability of HgO , Hg_xWO_3 bronzes have been elaborated under 3kb pressure ²

New lead (IV) compounds the preparation of which requires unstable lead dioxide such as the $\text{La}_2\text{Pb}_2\text{O}_7$ pyrochlore have been obtained in a similar way ³

High Pressure and Disproportionation

High pressure can hinder disproportionation and favour on contrary stabilization of intermediate states. Let us quote as an example chromium (IV) which is unstable in an octahedral site, disproportionating when heated at normal pressure into oxidation states III and VI $3\text{Cr(IV)} \rightarrow 2\text{Cr(III)} + \text{Cr(VI)}$, as oxidation state III is favored in an O_h surrounding by $t_{2g}^3 e_g^0$ configuration and o.s. VI by strong covalency within the CrO_4 tetrahedron. Nevertheless, under oxygen pressure chromium dioxide can be prepared either by hydrothermal reduction⁴ of CrO_3 or by oxidation⁵ of Cr_2O_3 . Due to its ferromagnetic properties CrO_2 is as acicular tiny particles a good magnetic taperecording material.⁶

High Pressure and Negative Variation of Unit Cell Volume

The preparation under pressure of rare earth monoxides has been investigated by Léger *et al*⁷

The Gibbs free energy ΔG corresponding to the synthesis $\text{Ln} + \text{Ln}_2\text{O}_3 \rightarrow 3\text{LnO}$ (Ln: rare earth) is positive at ordinary pressure for most rare earths, but negative for europium (this value explains why only EuO is stable in normal pressure conditions)

Under high pressure, resulting from a negative value of the unit cell volume ΔV , a $P\Delta V$ term can compensate the initial positive value of ΔG as far pressure is high enough. Such a phenomenon favours the synthesis of new rare-earth monoxides, e.g. SmO between 15 and 60 kb pressure.

High Pressure and Stabilization of Materials with Intermediate Properties

In preventing from certain lattice instabilities, high pressures are able to stabilize materials intermediate between those described by classical models.

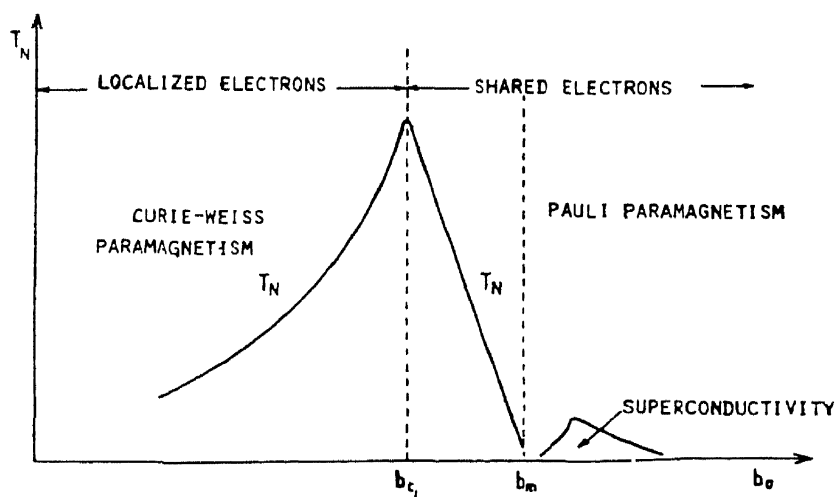


FIG 3 Plot of T_N against transfer integral b_σ for $n = 1(8)$

Let us quote the LnNiO_3 perovskites prepared under high oxygen pressure with properties ranging between those of insulating and metallic materials, a situation nature likes to by-pass in the absence of an appropriate driving force.

The localization of the e_g electron of low spin nickel (III) depends on the covalency of the $(\text{Ni—O})_\sigma$ bond as already shown by Goodenough from its (b_σ, T_N) diagram (Fig 3)

LaNiO_3 can already be prepared at atmospheric pressure with a small rhombohedral distortion.⁸ Due to large size of La^{3+} the overlapping of the nickel(III) σ -orbitals with the p orbitals of oxygen is nearly forming a 180° angle ($b_\sigma > b_m$ in Goodenough's diagram) and LaNiO_3 is metallic with a Pauli type paramagnetism

For the other LnNiO_3 perovskites high pressure is necessary to synthesize the stoichiometric oxides.⁹ Due to smaller size of the rare earth the distortion of the unit cell increases and the Ni—O—Ni angle decreases from 180° , all the more as Ln^{3+} is shrinking. Weaker orbital overlapping leads to disappearing metallic character. The lower covalency of the $(\text{Ni—O})_\sigma$ bonds accounts for the use of high pressures for the elaboration of the materials, which are no more thermodynamically stable under ordinary pressure. Table I illustrates the evolution of the Ni—O—Ni angles with the rare earth considered.¹⁰

TABLE I

Ni—O—Ni angles in the LnNiO_3 oxides of perovskite or perovskite derived GdFeO_3 structure (Ln rare earth)

	Along z-axis	In the xy plane
NdNiO_3	159.1°	159.5°
SmNiO_3	152.8	153.5
EuNiO_3	149.7	150.3
GdNiO_3	147.4	148.5
DyNiO_3	145.2	147.2
YNiO_3	142.9	145.4
ErNiO_3	142.1	145.4
TmNiO_3	142.4	145.2
YbNiO_3	141.3	144.7
LuNiO_3	140.2	143.5

As shown in Fig 4 the variation of reciprocal magnetic susceptibility vs temperature for YNiO_3 and LuNiO_3 (where the rare earths are diamagnetic) is consistent with a certain degree of electronic localization ($b_e < b_\sigma < b_m$). The slope is smaller nevertheless than that which would correspond to a perfect $t_{2g}^6 e_g^1$ localization ($b_\sigma < b_e$), a feature consistent with absence of a Jahn-Teller distortion in the lattice.

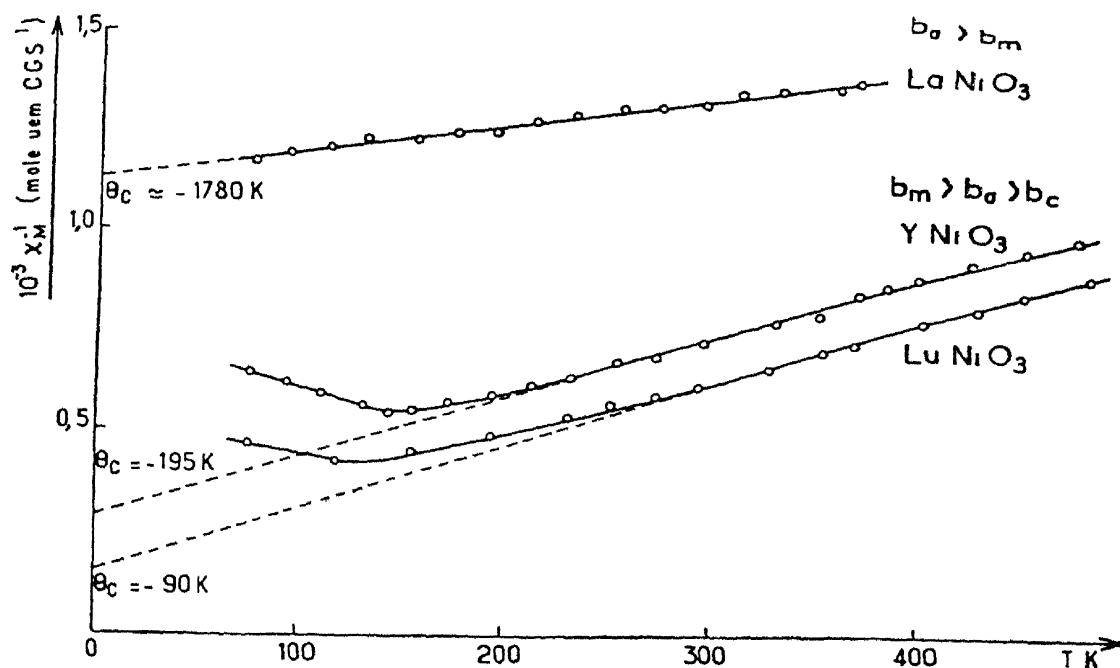


FIG 4 Variation of the reciprocal molar magnetic susceptibility vs temperature for the YNiO_3 , LaNiO_3 and LuNiO_3 phases

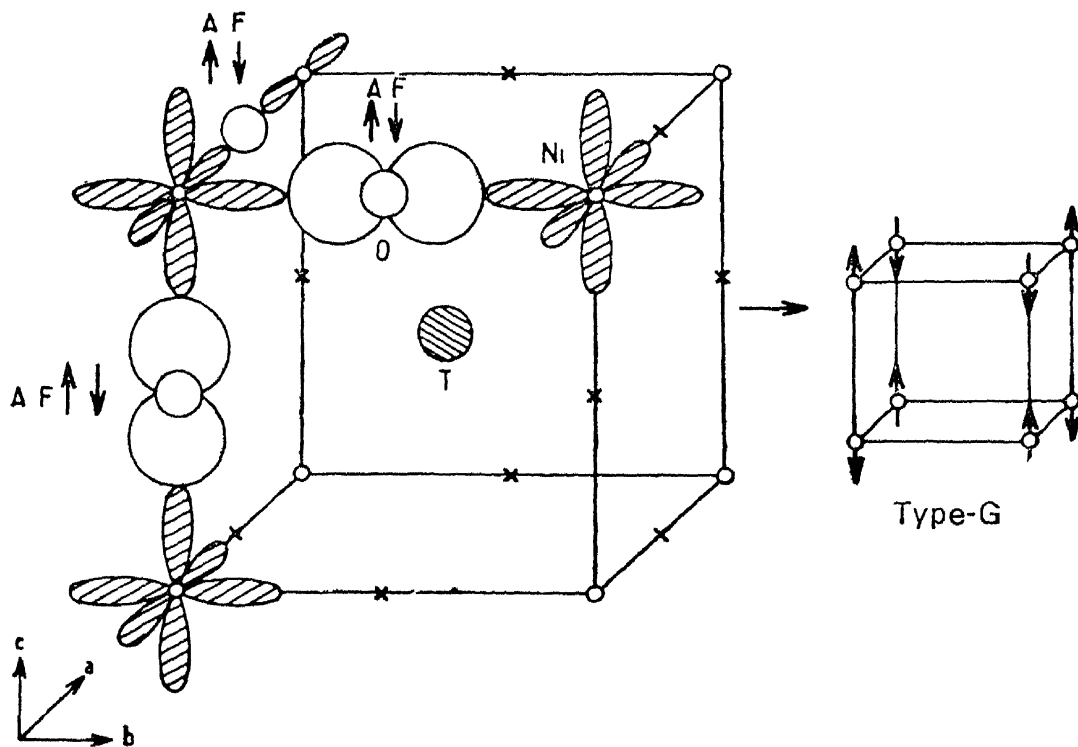


FIG 5 Suggested magnetic couplings for YNiO_3 and LuNiO_3

In fact in YNiO_3 and LuNiO_3 a uniform distribution of the e_g electron around Ni^{3+} appears, but without real delocalization in the whole lattice like in LaNiO_3 (Fig 5).

Attempts to synthesize at atmospheric pressure materials intermediate between insulators and Pauli paramagnetic behaviour lead mostly to disproportionation into two phases with respective insulating and metallic character

High Pressure and Stabilization of High Oxidation States

The preparation of unusual oxidation states of transition elements depends on the possibility of stabilizing the corresponding electronic configurations.

Using appropriate structural and chemical bonding factors, high oxygen pressure synthesis can lead to unusual high oxidation states.

This possibility is illustrated in a spectacular way by the stabilization of six-coordinated iron (V) which has been obtained recently for the first time in an oxide. Fe(V) had only been reported so far in oxides as traces or in tetrahedral coordination^{11,12,13}

With a $t_{2g}^3 e_g^0$ electronic configuration in an octahedral site, iron (V) has an isotropic electronic distribution ($^4A_{2g}$ ground term). Such an electronic configuration may fit very well with a site of O_h symmetry. But the high ionization potential of iron (V) requires a covalency of the Fe—O bonds strong enough to stabilize the $t_{2g}^3 e_g^0$ configuration.

Synthesis of an oxide containing Iron (V) is only possible under high oxygen pressure. Therefore, we had to select a structure able to be very stable under such conditions. The most convenient one, having both high stability and an O_h symmetry site, appeared to be the perovskite structure

To enhance the covalency of the Fe—O bond it was brought in competition with 6 weak Li—O bonds surrounding each FeO_6 octahedron (Fig. 6)

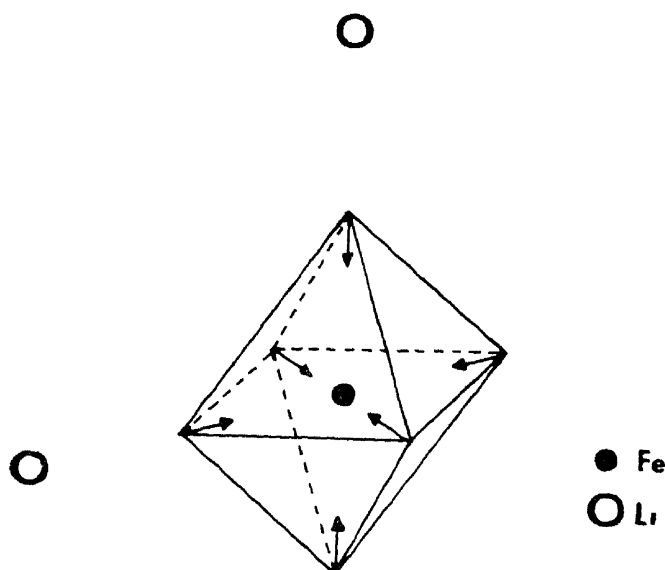


FIG. 6 Formation of a FeO_6 octahedron with iron (V) in $\text{La}_2\text{LiFeO}_6$

According to this prediction the $\text{La}_2\text{LiFeO}_6$ phase has been recently prepared under high oxygen pressure (70kb). Lanthanum was selected by reasons of size and charge¹⁴. The thermal decomposition *in situ* of unstable KClO_3 was used as an oxygen source in the sealed reaction tube. After quenching KCl was quickly leached out with water.

The new material has been characterized chemically and physically, in particular by magnetic measurements (Fig. 7) and Mossbauer spectroscopy (Fig. 8).

If we compare the various chemical shifts observed by the latter technique for iron in various oxidation states, the strongly negative value obtained appears to characterize both oxidation state V and strong covalency of Fe—O bonding.

ESR measurements have also shown an excellent agreement between the observed g -value in $\text{La}_2\text{LiFeO}_6$ ($g \approx 2.0135$) and the experimental one claimed

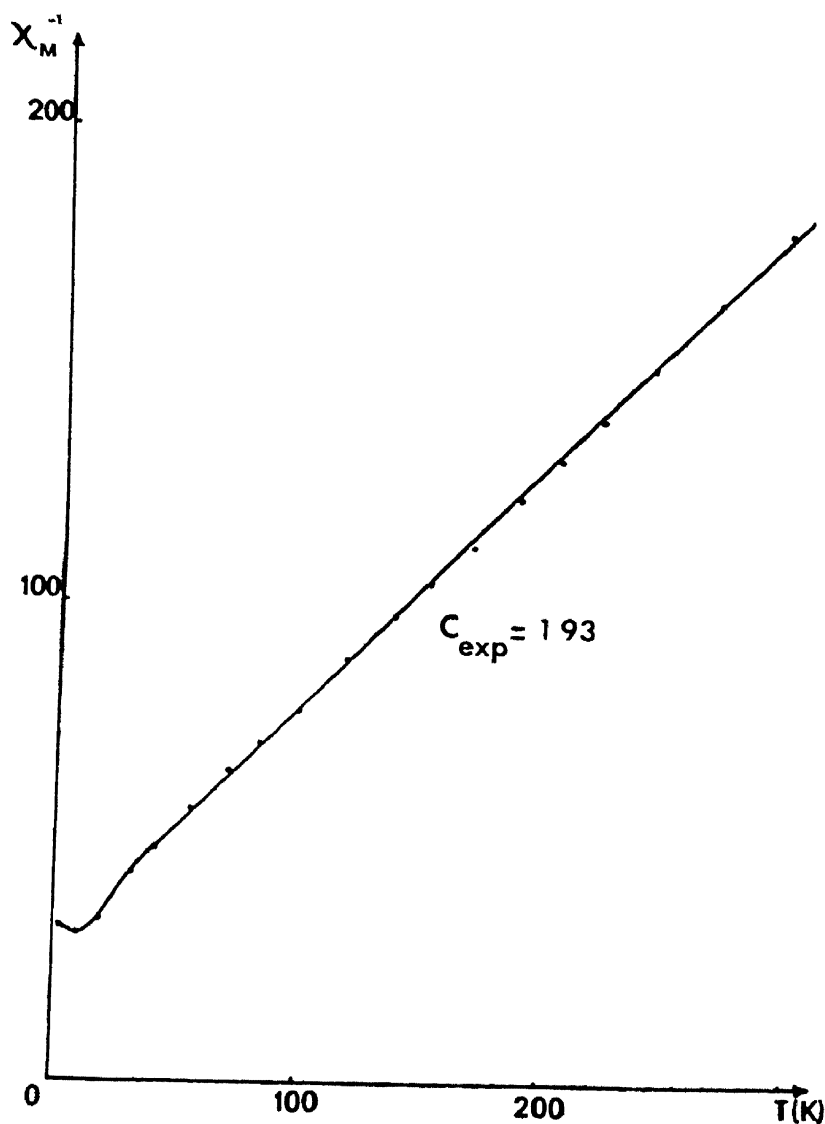


FIG. 7 Reciprocal molar susceptibility of $\text{La}_2\text{LiFeO}_6$ vs temperature characterizing formation of Iron (V)

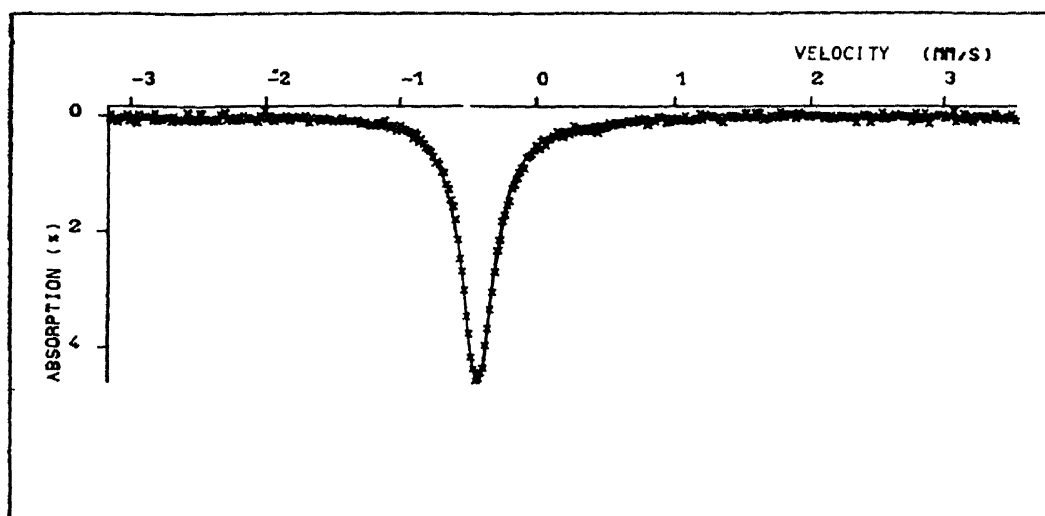


FIG 8 Mossbauer resonance spectrum of $\text{La}_2\text{LiFeO}_6$ at 293 K (source ^{57}Co in a rhodium matrix)

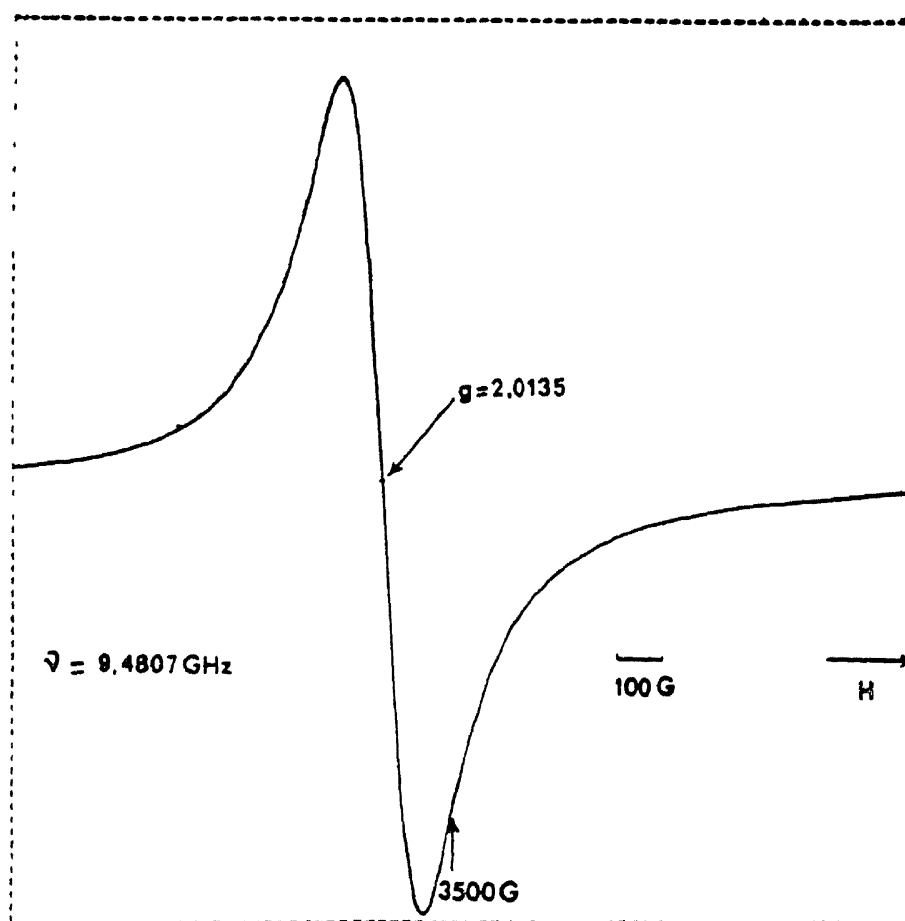


FIG 9 ESR spectrum of $\text{La}_2\text{LiFeO}_6$ at 293 K

before by Muller *et al* ($g \approx 2.0131$) for SrTiO_3 containing traces of Fe(V) as substitutional defects¹³ (Fig 9).

Let us mention that homologous $\text{La}_3\text{LiRuO}_6$ and $\text{La}_2\text{LiOsO}_6$ perovskites have been prepared even at ordinary pressure thanks to higher crystal field of ruthenium (V) and osmium (V) which are respectively $4d$ and $5d$ ions.

High oxygen pressures are obviously the best way for stabilizing unusual high oxidation states of transition elements, in particular $3d$ -elements (e.g. Fe(IV), Fe(V), Co(IV), Ni(III), Cu(III)). The most appropriate structures for obtaining given electronic configurations, for instance HS iron (IV) or LS nickel (III), can be predicted on hand of relatively simple models and effectively set up.¹⁵

High pressure fluorine leads in an analogous way to high oxidation state fluorides, e.g. Cs_2NiF_6 , Cs_2CuF_6 or $\text{Cs}_4\text{GaAgF}_{12}$.¹⁶

High Pressure and Elaboration of Defect-Free Entities

The use of fluids in supercritical conditions under high pressure allows elaborating almost defect-free single crystals either for basic research or even for industrial applications. A similar technique can be used for preparing tiny grains as a first step in ceramic formation processes. Absence of differences in superficial tensions avoids formation of microcracks and enhances strongly the mechanical properties of the ceramics.

As an example large size high quality single crystals of quartz can be easily prepared at 400°C under 1.5 kb pressure using polycrystalline quartz as starting material and an alkaline solution as transport fluid.¹⁷

STRUCTURAL TRANSFORMATIONS UNDER PRESSURE

High pressure increases the density of the materials and as a consequence decreases the interatomic distances. Hence, the steric or electrostatic interactions are enhanced. The materials evolve so as to minimize such effects.

High pressure structural transformations are quite important in connection with explanation of geological processes as well as applications (e.g. the graphite $\rightarrow$ diamond or boron nitride $\rightarrow$ borazon transformations).

In first approximation two types of transitions may be observed

- (A) those without increase in coordination number
- (B) those with increasing coordination

Without Increasing CN

The first transformation type can be illustrated by some significant examples :

- Structural transformation of the hexagonal perovskites.
- Structural transformation of the Li_2MF_6 fluorides

For the perovskites, the structural distortion depends closely on the Goldschmidt structural factor t . For $t = 1$ cubic symmetry is observed. When $t > 1$ hexagonal or rhombohedral varieties appear. For the largest t -values all layers have a hcp type-packing, all BX_6 octahedra share faces with each other to form chains parallel to the c -axis (2H structure).

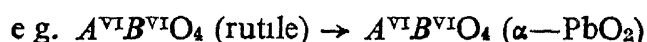
On the other hand, if the packing is of *cfc*-type, the octahedra form a three dimensional network sharing only corners and resulting in the well-known cubic perovskite structure ($t = 1$).

For intermediate t -values stackings having alternately *hc* and *cfc*-packed layers can exist (Fig. 10).

Under pressure, owing to the short cationic distances across the common faces of the octahedra and hence to strong electrostatic repulsion between the concerned B cations, an evolution from face sharing to corner sharing octahedra is observed: the number of blocks with face sharing octahedra decreases in the lattice: $2H \rightarrow 9H \rightarrow 4H \rightarrow 6H \rightarrow 3C$ structural transformations can be observed.¹⁸

Some of the intermediate phases may show ferromagnetic behavior as far appropriate magnetic cations occupy two different sites (for instance in 6H-type RbFeF_3).

Many other examples illustrate transformations without change of the coordination number, but with reduced cationic repulsion due to structural shifts:



For the Li_2MF_6 fluorides¹⁹ three structural types occur and the transformation from each other results from a modification of the positions of the cations in the *hc* lattice of the fluoride ions. The increase in the size of the M^{4+} ion as well as increasing pressure leads to stronger electrostatic repulsion. As a consequence decrease in the number of edges shared by the (MF_6) and (LiF_6) octahedra is observed.

As illustrated by Fig 11 transformations type I $\rightarrow$ type II $\rightarrow$ type III may be successively observed according to this rule. The number of common edges is successively 3, 2 and 0

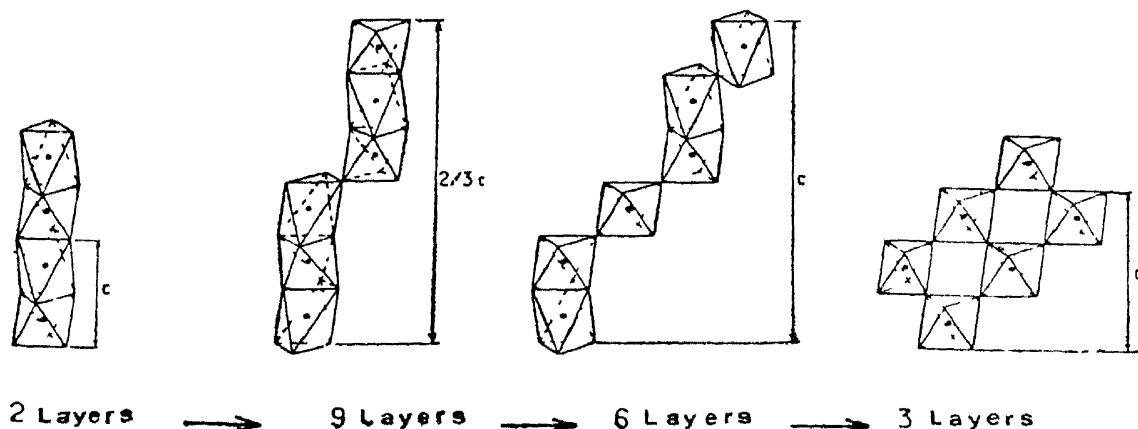
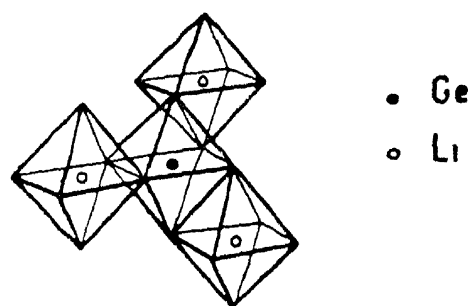
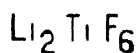
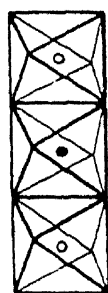


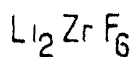
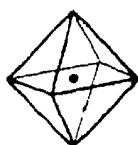
FIG 10 Structural evolution vs pressure for some ABX_3 polytypes—Increasing pressure gives rise to shift from left to right



TYPE I



TYPE II



TYPE III

FIG 11 Structural evolution vs pressure for the Li_2MF_6 fluorides (from type I to type III)

With Increasing CN

The examples of transformations under high pressure with increase in CN are numerous. Higher coordination increases the compactness of the lattice and is indeed favoured by pressure.

The phase transition recently observed for PdF_2 under pressure is a good illustration of this phenomenon. A large number of compounds with MX_2 general formulation derive from three main structural types: quartz, rutile and fluorite. They are characterized by the respective coordination number of cations and anions.

IV-II for quartz-type

VI-III for rutile-type

VIII-IV for fluorite-type

Concerning the d elements, if we consider the whole set of so far known MX_2 oxides and fluorides only ZrO_2 and HfO_2 show at atmospheric pressure a structure derived from the fluorite-type

The comparative stability of the rutile and fluorite-type structures depends primarily on the ratio of the cation/anion radii. For relatively small values of this ratio MX_2 compounds crystallize with the rutile structure and for the largest ones the stable form observed should be the fluorite-type. It is almost the case for the ZrO_2 and HfO_2 oxides, of baddeleyite type at low temperature (a structure actually close to that of CaF_2) and of fluorite-type at high temperature

Among the d element difluorides PdF_2 with rutile structure shows the highest $r_{M^{2+}}/r_{F^-}$ ratio and appears to be the most favorable compound to be investigated under high pressure conditions

Tressaud *et al*²⁰ have recently obtained a cubic high pressure form of PdF_2 , quenchable to room conditions¹⁹. The anionic environment of palladium $2+$ derives from that of the fluorite-type by a rhombohedral distortion of the fluorine cubes (Fig 12)

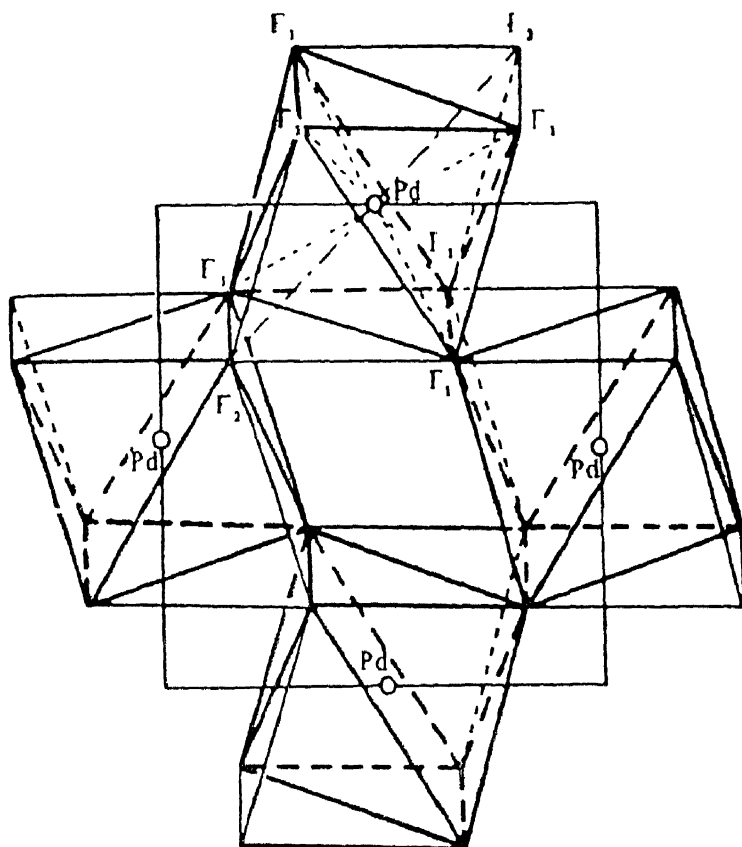


FIG 12 Structure of H P PdF_2 projection on a (001) plane of the anionic environment of Pd atoms at $z = 0.5$

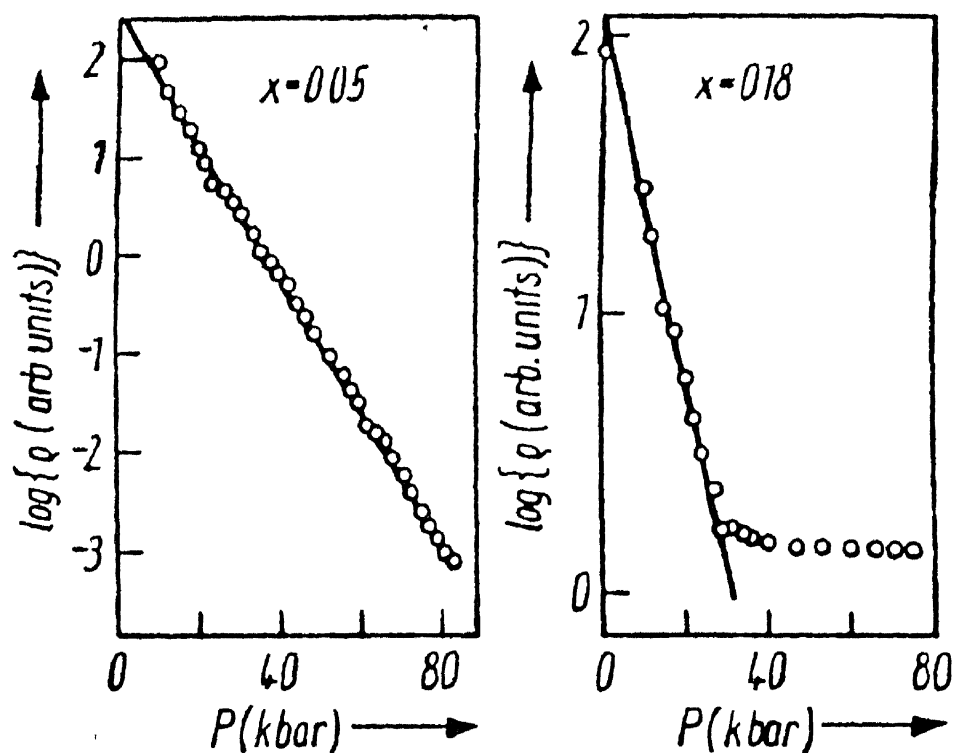


FIG 13 Variation of the logarithm of the resistivity with pressure at room temperature for $\text{Eu}_{1-x}\text{Nd}_x\text{O}_{1-x}$ ($x = 0.05$ and $x = 0.18$)

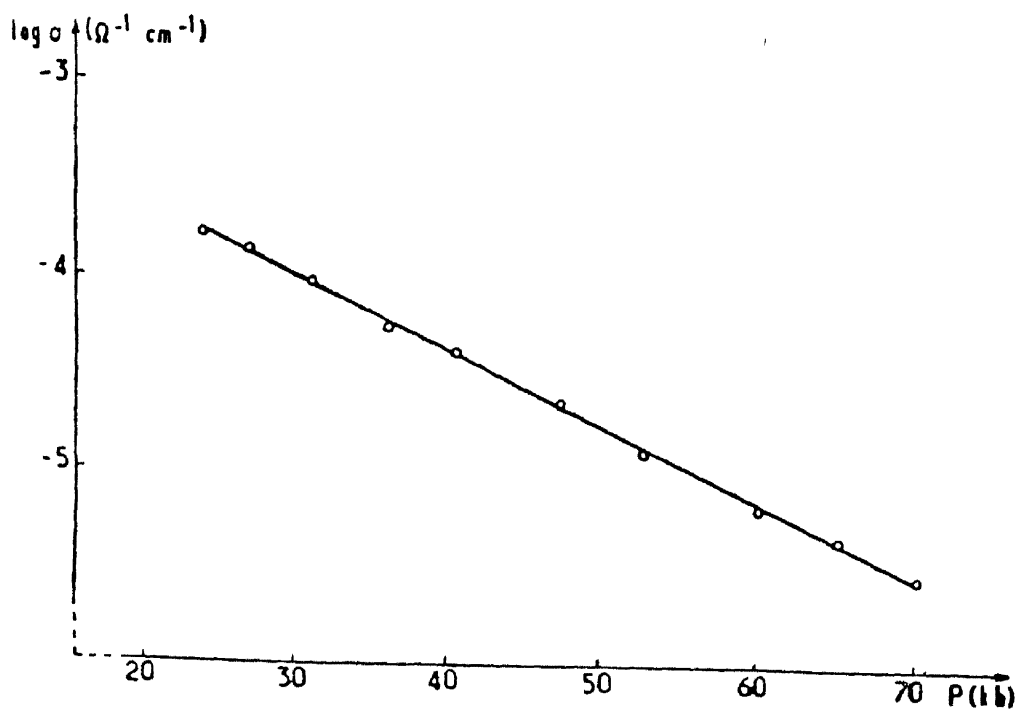


FIG 14 Variation of the logarithm of the conductivity with pressure at 300 K for PbSnF_4

EVOLUTION OF SOME PHYSICAL PROPERTIES UNDER PRESSURE

Many physical properties have been investigated under high pressure conditions, e.g.

- electronic conductivity
- ionic conductivity
- ferroelectric behaviour

They are all very sensitive to the cation-cation or anion-anion distances

The most famous result is the metallic behavior of solid hydrogen under very high pressure claimed by Vereshagin²¹

For EuO the promotion of a $4f$ electron into a $5d$ state due to broadening of the $5d$ band occurs at 300kb, leading to a non metal $\Rightarrow$ metal transition.²² The same phenomenon has been observed recently at lower pressure for rare earth oxynitrides $\text{Eu}_{1-x}^{2+}\text{Ln}_x^{3+}\text{N}_x\text{O}_{1-x}$ ²³ The introduction of $4f$ electrons into the $5d$ type-conduction band is all the more easy as x is higher due to stronger covalency and $5d$ band broadening (Fig 13).

For mobile ions in superionic conductors shrinking of the opening windows in the structural pathways with increasing pressure induces for most materials reduced ionic conductivity. Such a phenomenon has been observed recently for PbSnF_4 , the best so far known anionic conductor²⁴ (Fig. 14).

CONCLUSION

High pressure technique appears to be quite an efficient tool in solid state chemistry, not only for new fundamental investigations (new elaboration methods, structural transitions, semiconductor-metal transitions), but also in the development of novel materials or in the improvement of worthwhile properties. Owing to the fact that 90 per cent of the materials in the earth exist under pressures much higher than 100kb, high pressure is obviously also an important crossroad between different scientific areas and a factor of human progress.

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LOW-DIMENSIONAL FERROMAGNETIC COMPOUNDS : RECENT DEVELOPMENTS

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After an introductory survey of the unusual physical properties associated with low-dimensional lattices recent developments in the study of low-dimensional inorganic compounds with near-neighbour ferromagnetic exchange interactions are reviewed with special reference to work on magnetic structures and phase transitions carried out by the Oxford group. The structural circumstance leading to ferromagnetism through superexchange are noted, and bulk magnetic and neutron scattering experiments on each category are surveyed. Canted and incommensurate magnetic structures are described. Studies of the mechanism of the transition to long range order are summarized.

Key Words : Low Dimensional Compounds; Ferromagnetic Compounds; Incommensurate Structures; Magnetic Interactions

INTRODUCTION

ONE of the most important and influential developments in solid state chemistry in the last ten years has been the identification and study of compounds in which the major interactions between the constituent ions or molecules take place in fewer than three dimensions. Thanks to the ingenuity of organic and inorganic chemists, compounds have been made with properties that challenge theory, like one-dimensional metals, or with combinations of properties not previously found in association with one another, like ferromagnetism and optical transparency or superconductivity in molecular crystals. Some of the special properties associated with low dimensionality are displayed in Table I. Of course, low-dimensional materials like micas or graphite have been known for many years and hundreds, if not thousands of solids contain layers or chains of closely spaced atoms or ions. However, the adjective 'low-dimensional' has come into use principally to describe physical properties that arise from the collective behaviour of electrons on lattices confined to one, or to two orthogonal axes. Two simple examples will illustrate the point.

In 1955, Peierls¹ pointed out that a one-dimensional electron gas is inherently unstable with respect to any lattice distortion with periodicity $1/2 k_F$ equivalent to the wave-vector k_F at its Fermi Surface. This occurs because the energy of the occupied electron energy levels is lowered, and that of the

TABLE I

Some properties of low dimensional compounds

Property	Chain	Example	Layer
<i>Structures</i>			
Intercalation	$(\text{SN})_x\text{--Br}_2$	TaS ₂ NiPS ₃ FeOCl	+ amines or organometallics
Molecular composites		$(\text{C}_7\text{H}_{15}$  $\text{CH}_2\text{NH}_2)_2\text{MnCl}_4$ (gly-diac-gly) CdCl ₂	
Phase transitions in organic groups	$((\text{CH}_3)_4\text{N})\text{MnCl}_2$	$(\text{CH}_3\text{NH}_2)_2\text{CdCl}_4$	
<i>Magnetism</i>			
Low dimensional magnetism	CsNiF ₃	Mn stearate	
Metmagnetism	Co (pyridine) ₂ Cl ₂	FeCl ₂	
Transition to long range order	AFeCl ₃ (A = K, Rb, Tl, Cs)	$(\text{RNH}_2)_2\text{MCl}_4$ (M = Cr, Cu)	
<i>Conductivity</i>			
Molecular metals	Ni (porphyrin) I	Graphite and BN salts	
Peierls instability	$\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.30}3\text{H}_2\text{O}$	—	
Charge density wave	NbSe ₃	NbS ₂	
Superconductivity	$(\text{SN})_x$ $\text{Hg}_{1.86}\text{AsF}_6$	TaS ₃	

unoccupied ones raised, when the lattice periodicity is increased from a/n_e , where n_e is the fractional band filling (or average number of valence electrons per atom in the tight-binding approximation). A gap in the energy spectrum then opens at k_F and the lattice undergoes a transformation from metallic to semi conducting. The Peierls theorem is only exact in one dimension because the requirement of a unique k_F value is only satisfied under those conditions. Consequently, a search began in the 1970's for one-dimensional metals. Coordination chemistry provides some of the clearest examples, the mixed valency Pt chain compounds such as KCP ($\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.30}3\text{H}_2\text{O}$), and the predictions of Peierls were verified in detail ²

A second example is one-dimensional magnetism. It can be shown quite easily that a chain of localized moments interacting *via* near-neighbour ferro-or antiferromagnetic Ising exchange cannot exhibit infinite range order at any temperature above absolute zero, and hence, has no phase transition from an ordered to a disordered state. This is because the enthalpy required to reverse one spin in the otherwise completely ordered lattice is outweighed by the entropy gain arising from the fact that the spin reversal can take place at any site with equal probability. As I shall describe later in this article, the argument is

more subtle for other interaction Hamiltonians and higher dimensionality because, for example, 'domains' of reversed spins within three-dimensional lattice can have a wide variety of shapes, and hence domain boundary energies. Surprisingly good approximations to one-dimensional ferro- and antiferromagnets exist, the most widely studied being those with structures related to the hexagonal perovskite lattice, e.g. CsNiF_3 and $\text{N}(\text{CH}_3)_4\text{MnCl}_3$. In the latter, the mean field transition temperature estimated from the measured near-neighbour exchange constant is 90 K while the Neel temperature is only 0.83 K. The optical spectra also reveal the dominant role of short range order, even down to very low temperatures³

To engineer interaction pathways confined to one or two dimensions alone, one frequently has to construct chemically quite elaborate structures, as Table I shows. Quite unusual opportunities for new kinds of physical behaviour then arise. For example, the role of molecular librational modes in the electron-phonon coupling responsible for the superconductivity of charge transfer salts is quite unknown. Low dimensionality also provides a structural mechanism for combining inorganic continuous lattices with organic molecular ones. Thus an inorganic layer may have organic molecules bond to it ionically, covalently or by metal-ligand coordination to make what we have called a 'molecular composite'⁴. The potential therefore exists to combine within the same crystal properties characteristic of the inorganic solid state, such as cooperative magnetism, and those more familiar from organic molecular solids like mesomorphism or topochemically steered solid state polymerization.

Both in the matter of finding paradigm examples of soluble physical models, and in synthesising new compounds with unlooked for properties, there has been intense world-wide activity for number of years. Reviews may be found in Miller (1982) and Gillespie and Day (1985)^{5,6}. In this brief article, it will not be possible to give more than a selective summary of that part of our own recent work on low-dimensional solids concerning magnetic interactions, to illustrate the richness of phenomena being uncovered.

LOW-DIMENSIONAL FERROMAGNETS

Ferromagnetic near neighbour exchange is quite rare in insulators, and usually is found only when the topology of the lattice forces a cancellation of competing antiferromagnetic exchange pathways. This is more likely to be the case in low-dimensional lattices because there is then a smaller number of equivalent 'bonds' between neighbours, and a smaller number of effective second and third near neighbours. There are two types of cation-anion-cation pathway which give rise to ferromagnetic exchange by the conventional super-exchange mechanism, and we have studied numerous examples of each.

Within a basic dimeric unit the requirement that unpaired spins on the two metal ions should align ferromagnetically is achieved if they occupy orthogonal orbitals. Given that metal-ligand covalency is not negligible, the necessary

orthogonality can be assured in principle in either of two ways.⁷ The first requires that the cation orbitals containing the unpaired spins overlap orthogonal orbitals on the bridging ligand, and the second that spin density is delocalized from one cation through an intervening anion orbital to an unoccupied orbital on the other cation. The latter unoccupied orbital is necessarily orthogonal to the other orbitals of the d -subshell that contain the remaining unpaired electrons. For the case of d -orbitals overlapping ligand p -orbitals these two situations are shown in Fig. 1

To engineer orthogonality between two d -orbitals of identical point symmetry on neighbouring lattice sites, of the kind shown in Fig 1(b), the principal axes of the ligand fields around the two sites must themselves be orthogonal. This is realized most effectively through the mechanism of a cooperative Jahn-Teller distortion, the $3d^9$ and high spin $3d^4$ configurations being the ones most subject to such distortion. K_2CuF_4 was the first example of a crystal which become ferromagnetic by this mechanism (T_c 6.4K).⁸ Based on the K_2NiF_4 structure, alternate corner-sharing octahedra are elongated along $[100]$ and $[010]$, ensuring that the half filled x^2-y^2 on one site is orthogonal to x^2-y^2 on each of its neighbours. Our own work has concerned the corresponding Cr(II) compounds A_2CrX_4 , where $A = Rb, Cs, RNH_3$ and $X = Cl, Br, I$.⁹ Here the problem is more complicated because the unpaired electron in the $e_g(O_h)$ subset occupies z^2 in an elongated D_{4h} site, and the three other electrons of the $3d^4$ configuration occupy xz, yz, xy . The z^2 orbital on site a (Fig 2) overlaps with a $p\sigma$ orbital on the bridging halide ion, which in turn overlaps x^2-y^2 on site b

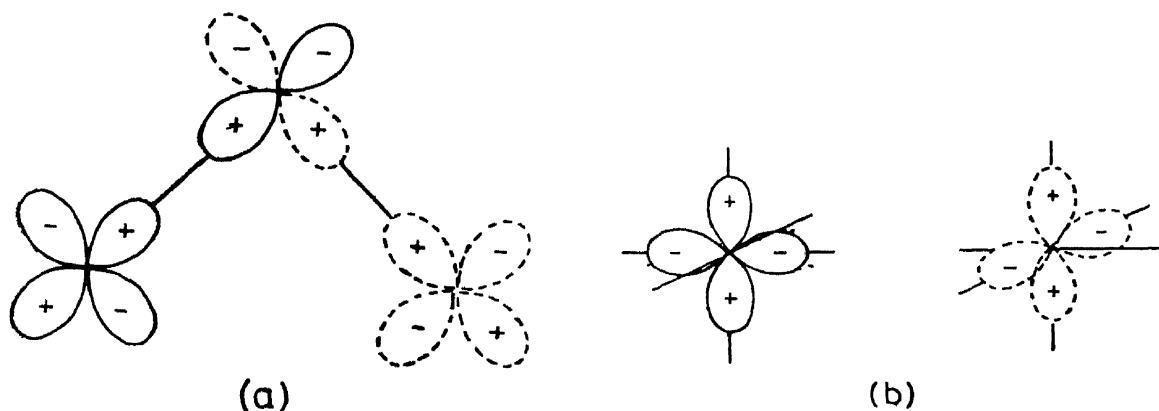


FIG 1 Two ways of achieving orthogonality between d -orbitals on adjacent metal ions (a) Orthogonal orbitals on the bridging anion, (b) orthogonal d -orbitals

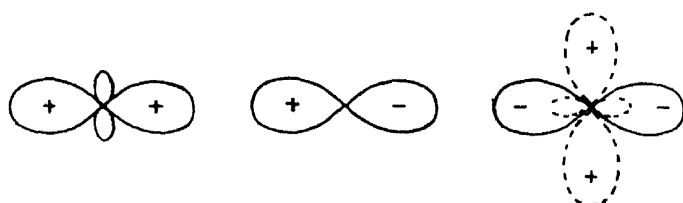


FIG 2 Superexchange pathway in A_2CrX_4 salts

Repulsion between the four unpaired electrons on site b and the spin density in x^2-y^2 transferred from site a is minimized if they are all parallel, hence the exchange constant J_{ab} is again positive.

To test this orbital ordering model we have performed single crystal polarised neutron diffraction measurements on Rb_2CrCl_4 at 4.5 K.¹⁰ Magnetic structure factors F_M were derived from the flipping ratios of 660 main structure reflections, whose intensity is derived mainly from the Cr^{2+} and Rb^+ sites and 57 'superlattice' reflections, whose intensity derives from the displacement of the basal plane Cl^- ions by the cooperative Jahn-Teller distortion. The F_M were modelled by representing the magnetization density as a superposition of densities from $3d$ and $4s$ -orbitals on Cr^{2+} and $3s$ and $3p$ centred on Cl^- . As well as allowing the total $3d$ and $4s$ moments on Cr^{2+} to vary in the least squares refinement, the proportion of the $3d$ moment residing in each of five orbitals was also refined with the following result yz 0.26(2), xz 0.25(2), xy 0.25, z^2 0.25(2) and x^2-y^2 -0.01(2). Thus the orbital ordering model is completely vindicated. In addition to the moment localized on the Cr^{2+} ($3.16\mu_B$ in $3d$ and $0.6\mu_B$ in $4s$) a small spin transfer to the Cl^- was also detected, amounting to $0.06\mu_B$ on those lying in the basal plane and $0.08\mu_B$ on those in the axial sites.

The ground state in the $A_2\text{CrX}_4$ compounds has $S = 2$, instead of $S = 0$ for K_2CuF_4 , and J is somewhat larger because of increased metal-ligand covalency, which arises partly from the heavier halogen and partly from the larger radial extension of the $3d$ -orbitals nearer the beginning of the d -block. Consequently T_c is increased to the region of 50 K. Wide chemical variation is possible within the $A_2\text{CrX}_4$ series, and representative values of J and T_c are shown in Table II. One of the most significant variations is in the interlayer separation, tuned by the organic sidechain R in RNH_3^+ , and these are also listed in Table II. Below, we shall discuss the nature of the phase transition in these two-dimensional lattices.

TABLE II

Exchange parameters, Curie temperatures and inter-layer spacings in two-dimensional ferromagnetic tetrachlorochromate (II) salts

	J/K	T_c/K	Interlayer spacing
Rb_2CrCl_4	14.4	52.4	7.88
$\text{Rb}_2\text{CrCl}_3\text{Br}$	—	55.0	8.03
$\text{Rb}_2\text{CrCl}_3\text{Br}_2$	—	57.0	8.19
$\text{Rb}_2\text{CrCl}_2\text{I}_2$	—	61	8.68
$(\text{CH}_3\text{NH}_3)_2\text{CrCl}_4$	13.0	42.0	9.44
$(\text{CH}_3\text{CH}_2\text{NH}_3)_2\text{CrCl}_4$	10.1	41.0	10.71
$(\text{CH}_3(\text{CH}_2)_2\text{NH}_3)_2\text{CrCl}_4$	9.3	39.5	12.35
$(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{CrCl}_4$	10.6	37.0	15.71
$(\text{CH}_3(\text{CH}_2)_4\text{NH}_3)_2\text{CrCl}_4$	9.3	—	17.81
$(\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3)_2\text{CrCl}_4$	10.6	—	—
$(\text{CH}_3(\text{CH}_2)_{11}\text{NH}_3)_2\text{CrCl}_4$	9.6	—	31.0

The second mechanism for achieving near-neighbour ferromagnetic exchange in Fig 1 requires a cation-anion-cation bridging angle in the region of 90° . The best approximations to such a situation in low-dimensional continuous lattice compounds are found in two major classes of compound, the one-dimensional hexagonal perovskites ABX_3 and the layer salts with $CdCl_2$ or CdI_2 structures. In all the halides MX_2 ($M = Fe, Co, Ni, X = Cl, Br, I$) J is ferromagnetic, though the much weaker interlayer exchange J' is antiferromagnetic, so the three-dimensional magnetic structure is of the metamagnetic type. The octahedral BX_6 unit in ABX_3 share opposite faces, so the $B-B$ distance is quite small and direct exchange, rather than superexchange is sometimes more important. Nevertheless, positive J is found in compounds with $B = Fe$ and Ni though the sensitivity of the ordering mechanism may be judged from Table III, which indicates the sign of J in ABX_3 ($B = Fe, Ni$) as a function of A and X .

TABLE III

Sign of the nearest neighbour exchange constant in hexagonal perovskites ABX_3 ($B = Fe, Ni$)

		<i>Fe</i>		<i>Ni</i>	
	<i>X</i> = Cl	Br	F	Cl	Br
<i>A</i> = K	+	—		—	
Rb	+	—		—	—
Cs	+	—	+	—	—
$N(CH_3)_4$			.	+	+

Competition between direct exchange, and competing 90° and 180° $B-X-B$ superexchange in these compounds is demonstrated quite neatly by examining the effect of hydrostatic pressure on the magnetic order. Thus in $RbFeCl_3$ with a Fe-Cl-Fe angle of 74.6° J is ferromagnetic while in $RbFeBr_3$, where it is 72.4° J is antiferromagnetic. Applying a hydrostatic pressure of 5Kbar to the former reduces the Fe-Cl-Fe angle below the corresponding angle in the bromide, yet J remains ferromagnetic and T_N increases from 2.5 to 6.5 K because anti-ferromagnetic interchain coupling increases¹⁴

COMPETING INTERACTIONS CANTED AND INCOMMENSURATE STRUCTURES

Nature rarely provides compounds in which a near-neighbour ferromagnetic exchange is the only interaction bringing about long range order. In practice, single ion anisotropy, dipolar interaction between chains or layers ordered spins, and exchange between more remote ions may all contribute to complicate the situation and introduce unusual types of order. In this section, a few examples from the work of our group on low-dimensional ferromagnets will be summarized.

As already noted, the single ion ground state in the A_2CrX_4 ferromagnet is a quintet (^5A_g in the D_{2h} crystal field). Therefore, in contrast to K_2CuF_4 , single ion anisotropy must be included in the hamiltonian. The principle axes of the g -tensors

on neighbouring sites are orthogonal because of the cooperative Jahn-Teller distortion and so also are the planar anisotropy terms. In the absence of exchange alternate Cr^{3+} moments would be directed along $[100]$ and $[010]$ of the parent K_2NiF_4 -type cell. The ferromagnetic near-neighbour exchange rotates the moments towards the easy $[110]$ direction but competition with the single ion anisotropy ensures that the moments retain a small ($\sim 3^\circ$) canting alternately to one side and the other of this axis (Fig. 3). The canting reveals itself by the presence of very weak purely magnetic reflections in the neutron diffraction,¹⁰ and by a small anisotropy gap in the spin-wave density-of-states at the centre of the Brillouin zone, which has important consequences for the behaviour of the optical absorption spectrum at very low temperatures. It also affects the critical behaviour, described later.

Another form of competition between ferromagnetic exchange and single ion anisotropy occurs in the one-dimensional hexagonal perovskites $A\text{FeCl}_3$ ($A = \text{Rb}, \text{Cr}$) where the dominant octahedral component of the crystal field gives a single ion ground state $^5T_{2g}$. First-order spin-orbit coupling lifts the degeneracy to leave a $J = 1$ level lying lowest, and this is further split by a more minor trigonal crystal field component into $M_J = 0$ and ± 1 . In contrast to the situation in the two-dimensional FeCl_2 , the singlet lies lower in energy than the doublet. Hence in the absence of an exchange field, or an externally applied field, the ground state is non-magnetic. The exchange field due to the near-neighbour ferromagnetic coupling induces mixing between the $M_J = 0$ and ± 1 levels which, if large enough, can

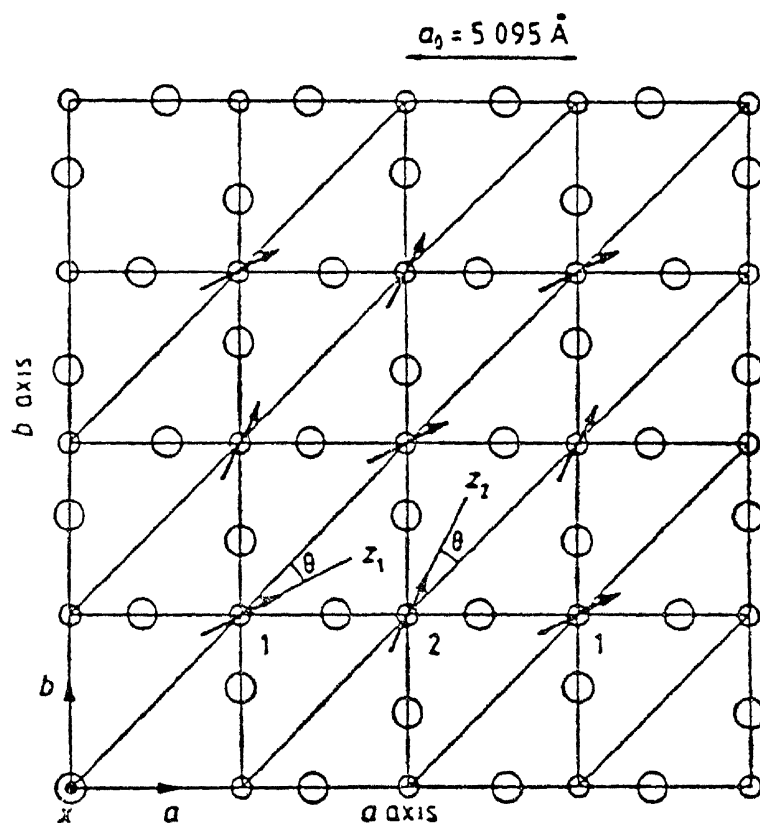


FIG 3 The canted spin structure of Rb_2CrCl_4

lead to a long-range-ordered magnetic ground state. As noted above, J depends on the Fe-Cl-Fe angle, which also determines the singlet-doublet separation. The nature of the long range order is therefore extraordinarily sensitive to small changes in the structure. For example RbFeCl_3 undergoes a transition to three-dimensional order, with easy-plane ferromagnetic chains, at 2.55K while CsFeCl_3 has no such transition down to 80mK. On the other hand order can be induced in the Cs compound by an applied field. Thus the magnetic phase diagrams of these two compounds are quite different, as shown diagrammatically in Fig. 4.

In a compound containing chains of ferromagnetically ordered spins like RbFeCl_3 , the ordering between chains is determined by yet another kind of competition. Weak antiferromagnetic coupling alone between chains would lead to a 120° (triangular) arrangement of spins in the plane perpendicular to the chains, signalled by magnetic neutron scattering intensity at $(1/3, 1/3, 0)$ with respect to the 'chemical' unit cell. However, since the chains are ferromagnetic, they act as giant dipoles, between which the free energy is minimized if the dipoles are collinear. Consequently, on passing $T_N = 2.55\text{K}$, neutron scattering intensity appears first at $(1/3 + \delta, 1/3 - \delta, 0)$ with $\delta \sim 0.018$, then moves to $(1/3 - \delta', 1/3 - \delta', 0)$, ($\delta' = 0.005$) at 2.35K and finally to $(1/3, 1/3, 0)$ at 1.9K.¹³ An example of the scattered intensity distribution in the a^*b^* plane is given in Fig. 5(a).¹⁴ For a RbFeCl_3 crystal doped with 5 per cent Cs^+ and the quite comparable evolution of the incommensurate ordering in CsFeCl_3 as a function of applied field in Fig. 5(b).¹⁵

Finally, a more classical source of incommensurate magnetic ordering is the competition between first, and more remote, neighbour exchange constants of opposed sign. For a two-dimensional triangular lattice Rastelli *et al*.¹⁶ calculated the relative stabilities of different spin structures as a function of $j_n = J_n/J_1$, with the result shown in Fig. 6. Clearly, when J_1, J_2 and J_3 (defined for the CdCl_2 lattice in Fig. 7) are all positive, as in the top right hand quadrant of Fig. 6, the order is simply ferro-magnetic (phase I). This is the situation in CoX_2 ($X = \text{Cl}, \text{Br}, \text{I}$)

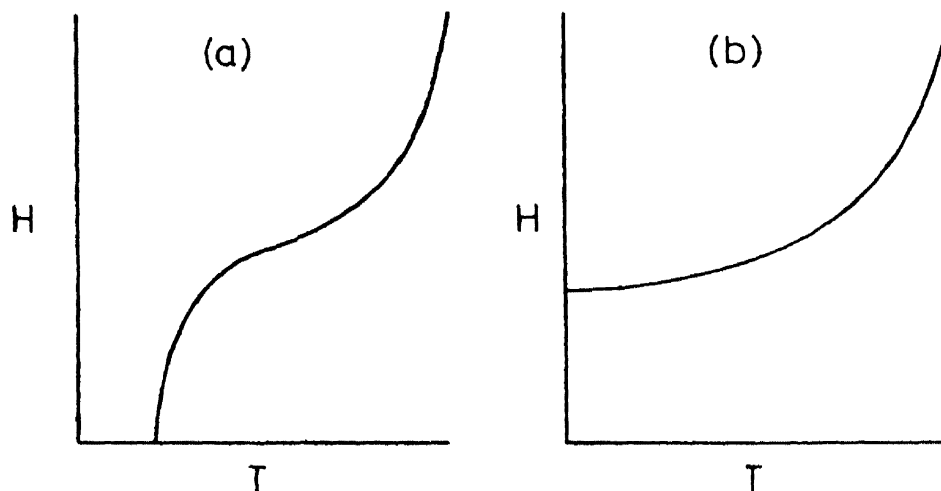


FIG. 4 Magnetic phase diagrams in the H, T plane for (a) RbFeCl_3 , (b) CsFeCl_3 .

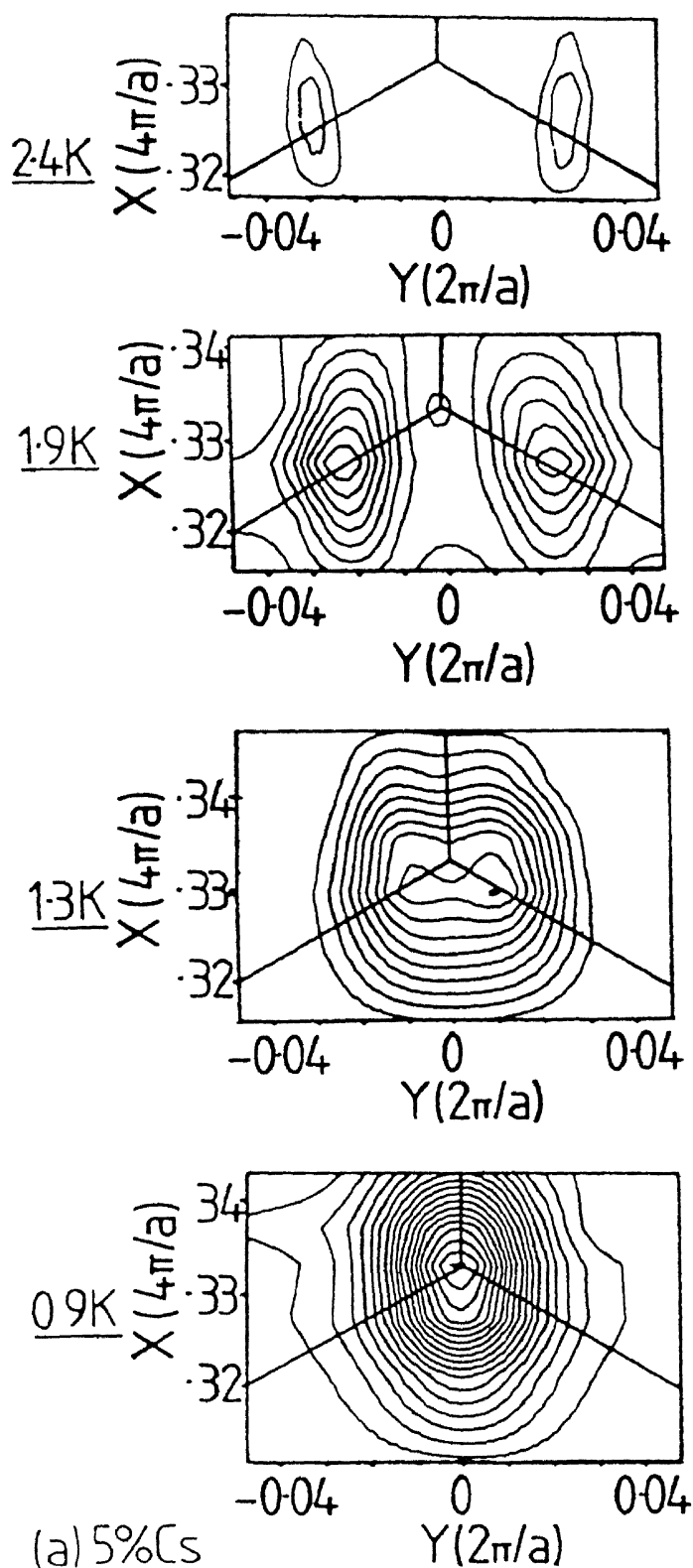


FIG 5 Incommensurate magnetic structures of RbFeCl_3 (a) Neutron scattering profile around $(1/3, 1/3, 0)$ in RbFeCl_3 at 2.2K¹⁴

and NiCl_2 . However, exceptionally in NiBr_2 $j_3 = -0.28$ and $j_2 \sim 0$, placing it within the stability range of a helical phase with propagation vector τ along $[110]$

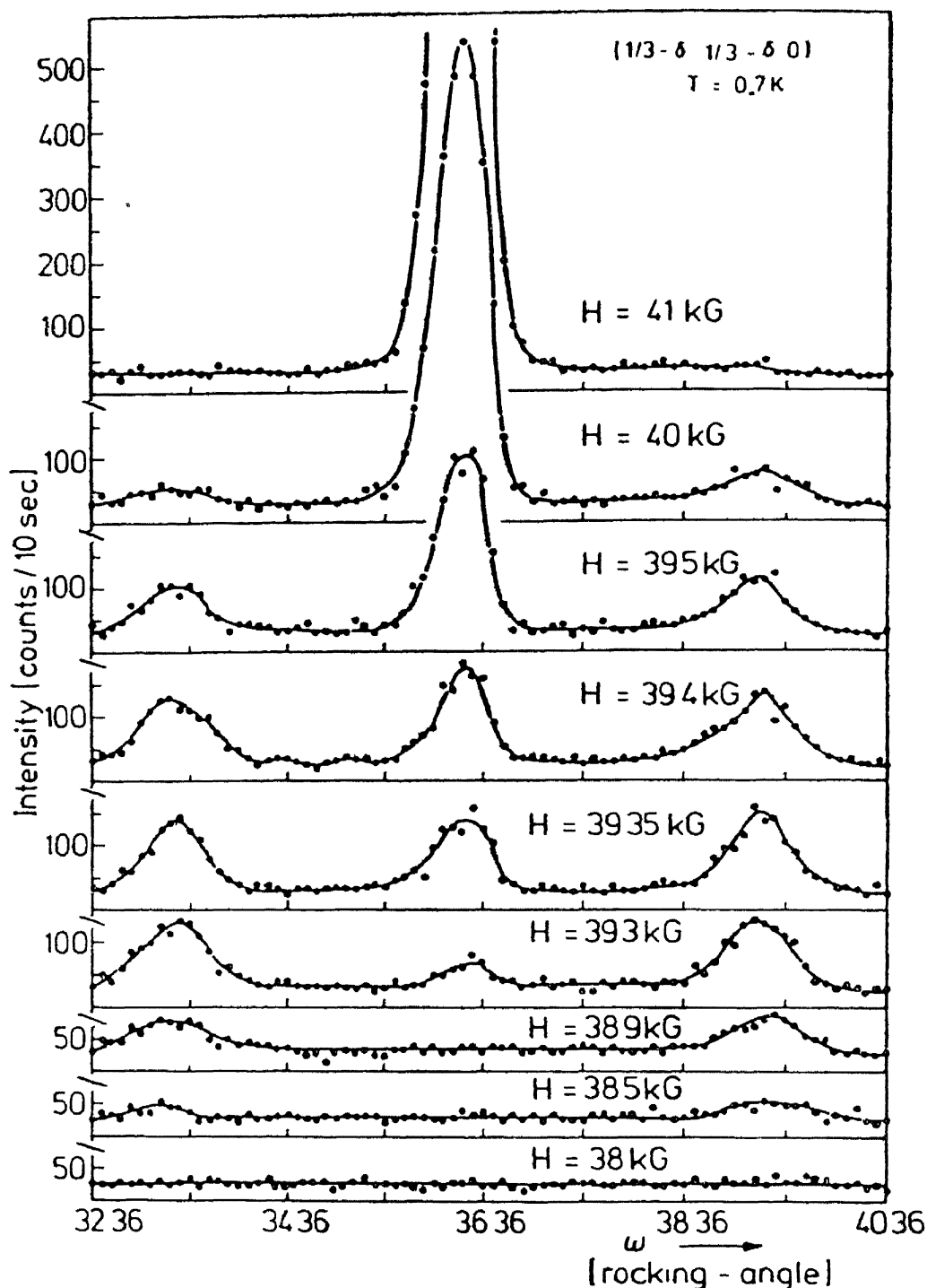


Fig 5 (b) Evolution of neutron scattering intensity at $(1/3-\delta, 1/3-\delta, 0)$ in CsFeCl_3 as a function of field ¹⁵

(phase IV, Fig 6) very close to the boundary with phase I. Single crystal neutron diffraction at 4K, using a multidetector to sample a region of reciprocal space around the $(0, 0, 3/2)$ reciprocal lattice point, reveals the resulting incommensurate structure with $\tau = 0.027$ (Fig 8(a)) ¹⁷. Remarkably, substituting NiBr_2 with 9 mole per cent Fe^{2+} causes τ to move to $[100]$ (phase III) (Fig 8(b)) ¹⁸.

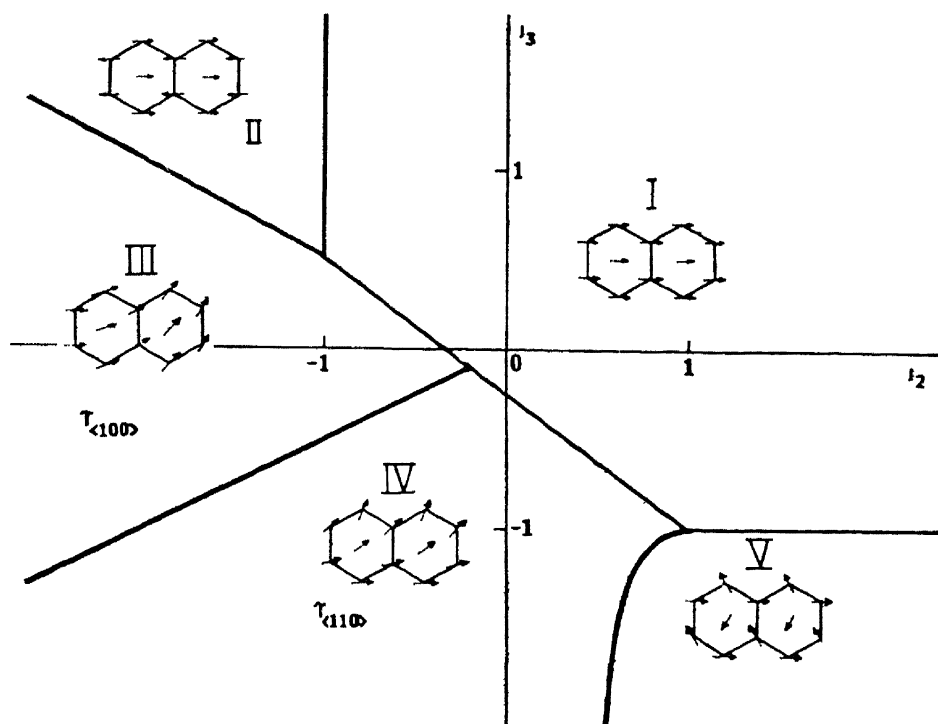


FIG 6 Magnetic phase diagram of a hexagonal planar lattice in the (j_2, j_3) plane,¹⁶ where $J_n = J_n/J_1$.

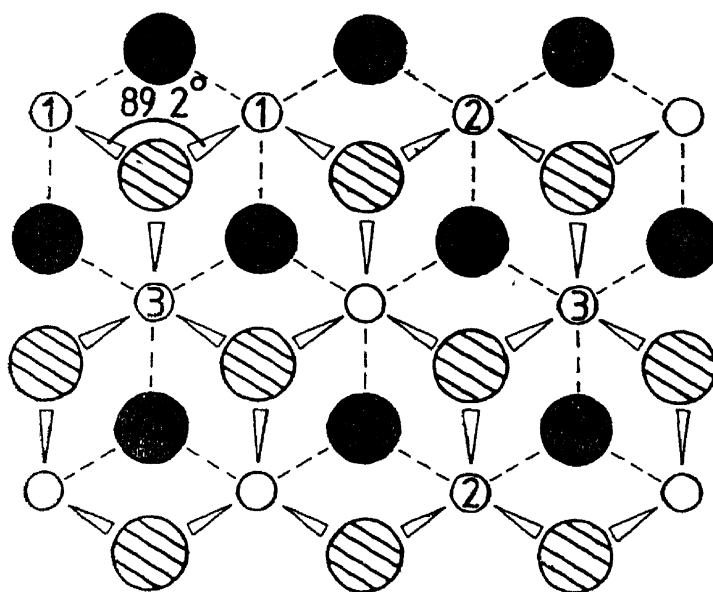


FIG 7 Intraplanar exchange constants J_n between (n, n) pairs in NiBr_2

An even more remarkable feature of NiBr_2 is that the propagation length, measuring the 'pitch' of the helix, increases continuously with increasing temperature until at 23K it has become infinite¹⁹ i.e the moments are collinear as in Phase I. The collinear phase then remains stable up to $T_N = 44\text{K}$. Again, single crystal neutron diffraction provides the evidence for the phenomenon. Fig 9 shows the

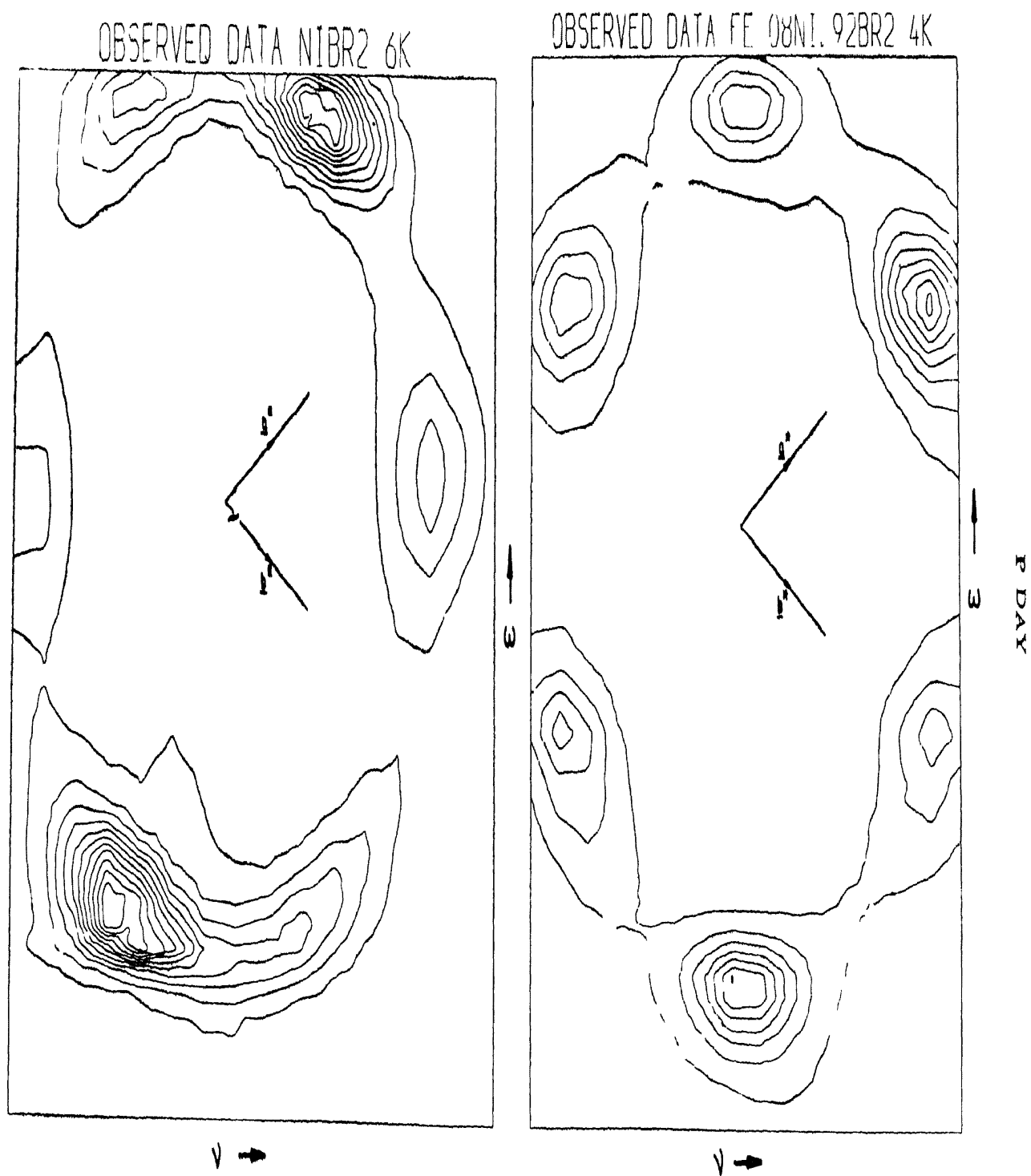


Fig 8 Neutron scattering intensity in the a^*b^* plane around $(0, 0, 3/2)$ at 4.2K in (a) NiBr_2 (b) $\text{Ni}_{0.98}\text{Fe}_{0.02}\text{Br}_2$.

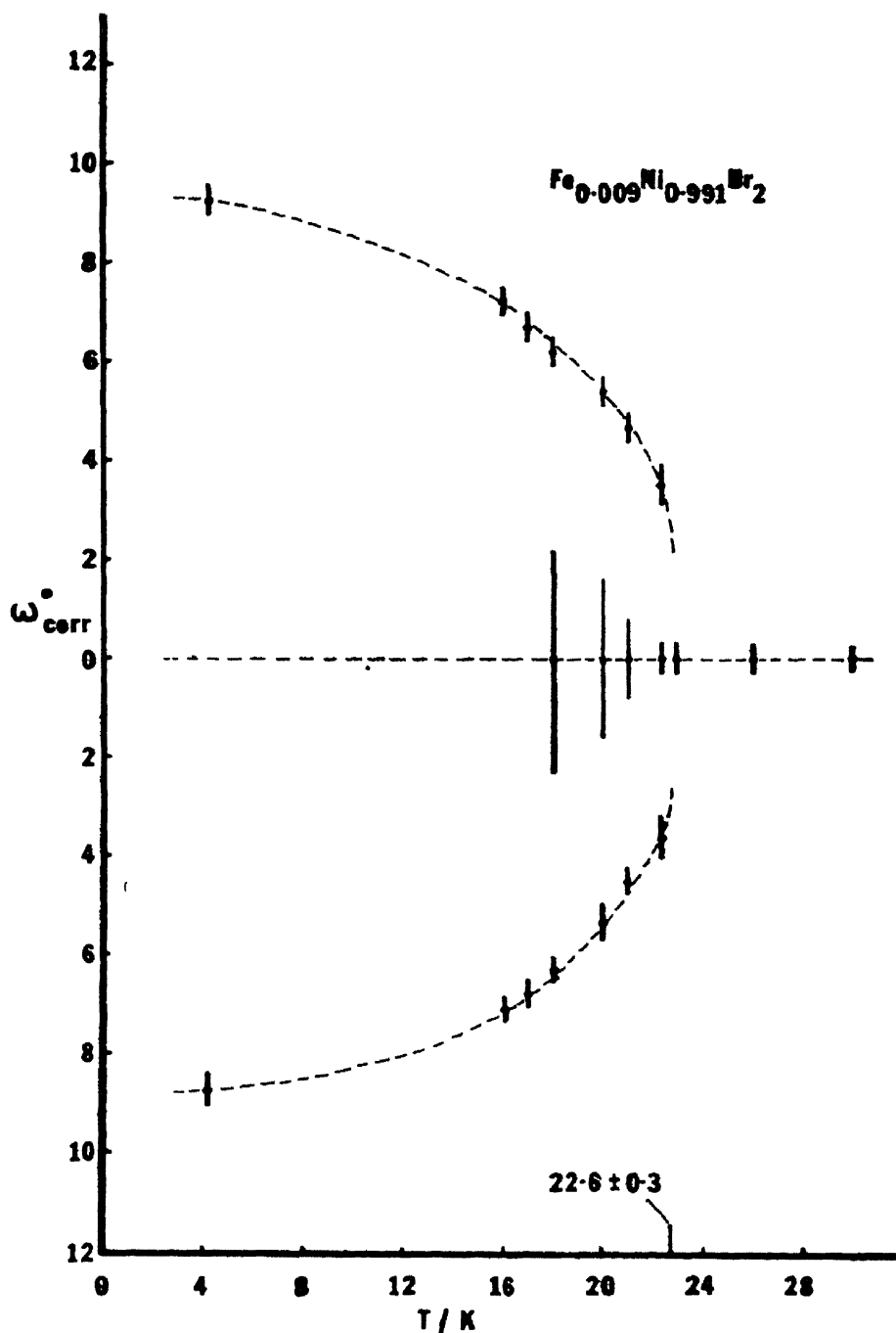


FIG 9 Temperature-dependence of the incommensurate propagation vector τ in $\text{Ni}_{0.99}\text{Fe}_{0.01}\text{Br}_2$ ¹⁸

temperature dependence of τ , in a NiBr_2 crystal containing 1 mole per cent Fe^{2+} , in which τ still lies along [110]. So far as is known, such behaviour is unique among magnetic insulators with localized moments, and at once raises the question 'what is its mechanism?' Lattice expansion would be a possible explanation since the J_n ratios might be modified sufficiently for the system to cross the boundary from phase IV to phase I. However, this can be ruled out by performing neutron diffraction measurements under hydrostatic pressure.²⁰ With increasing pressure τ decreases, so the decrease in τ with increasing temperature cannot be due to an

increase in the lattice parameters. We have also measured the dispersion of the spin waves in NiBr_2 along [110], [100] and [001] by inelastic neutron scattering at 4K, when the magnetic structure is helical, and 30K when it is collinear²¹ No significant variation is found in any of the intralayer exchange constants, though there is a small decrease in the anisotropy constant and the interlayer exchange constant. A theoretical explanation of this very unusual phenomenon has recently been given by Rastelli and Tassi²² in terms of magnon-magnon interactions

THE TRANSITION TO LONG RANGE ORDER

A fundamental question in any low-dimensional magnetic system concerns the mechanism of the transition to the long range ordered state. As mentioned in the Introduction, a one-dimensional array of Ising spins is predicted to have no long range order above 0 K and the same is true of a two-dimensional Heisenberg ferromagnet. On the other hand the two-dimensional Ising ferromagnet was shown to be capable of having a phase transition at finite temperature by Onsager²³. In contrast the two-dimensional XY model (i.e. of spins constrained within a plane) was only tackled theoretically much more recently. Kosterlitz and Thouless²⁴ (KT) showed that a phase transition in such a structure could occur at a temperature T_{KT} by the binding of pairs of vortices of spins with opposite chirality. A vortex is a system of spins constrained to rotate in the plane of the lattice. An example of a Monte Carlo simulation of the equilibrium spin configuration in an XY ferromagnet at $0.5T_c$ is given in Fig 10,²⁵ where the vortices of rotated spins are enclosed by the broken lines. For any temperature below T_{KT} the KT theory requires that

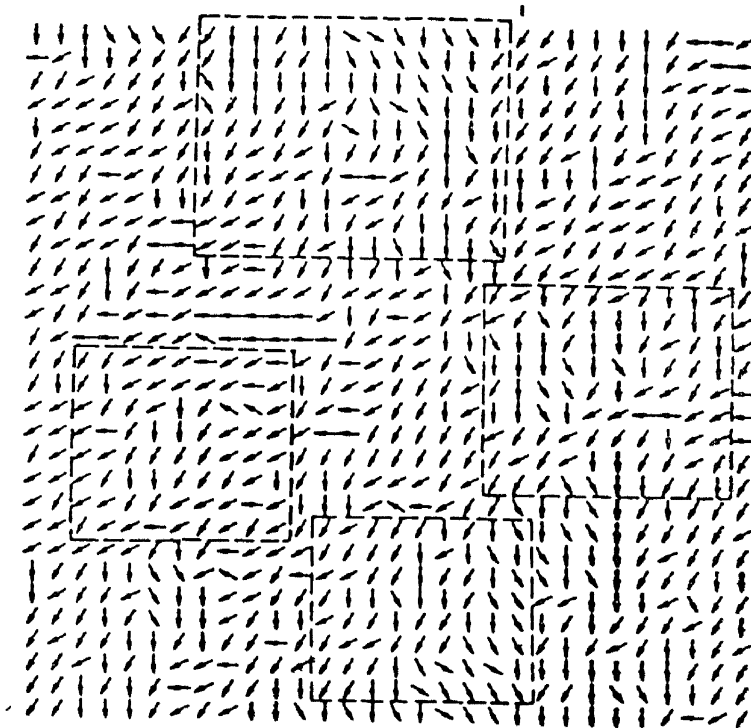


FIG 10 Monte Carlo simulation of spins in a two-dimensional XY lattice at $T = 0.5T_c$.²⁵

the susceptibility χ remains infinite. Therefore, all temperatures less than T_{KT} are critical and the magnetization should obey the relation.

$$\lim_{H \rightarrow 0} \langle M \rangle \propto H^{1/\delta(T)} \quad \dots (1)$$

Although they retain a very small anisotropy within the basal plane the A_2CrX_4 compounds are expected to be quite good approximations to two-dimensional XY ferromagnets. Fig 11 shows the magnetization of a single crystal of Rb_2CrCl_4 vs field along the easy [110] direction at temperatures between 6.6 and 79 K, measured by Faraday magnetometry²⁶. It can be seen that eq (1) is indeed obeyed up to 47 K. The variation of the exponent $\delta(T)$ with temperature is also in accordance with the prediction of the KT theory.

The experimental signature of KT theory at temperatures above T_{KT} is a divergence of χ according to the formula

$$\chi(T) = A \exp(B^*t^{-1/2}), \quad \dots (2)$$

where $t = (T - T_{KT})/T_{KT}$. This should be contrasted with the conventional power law theory of critical exponents,²⁷ from which one would predict

$$\chi^T = C(t_+)^{-\gamma}, \quad \dots (3)$$

where $t = (T - T_c)/T_c$. For Rb_2CrCl_4 we find that the high temperature susceptibility fits eq (2) very well (goodness of fit parameter $\chi^2_G = 9.6$) though nearly as good a fit can be obtained with eq. (3) ($\chi^2_G = 13.1$). Further verification of the KT

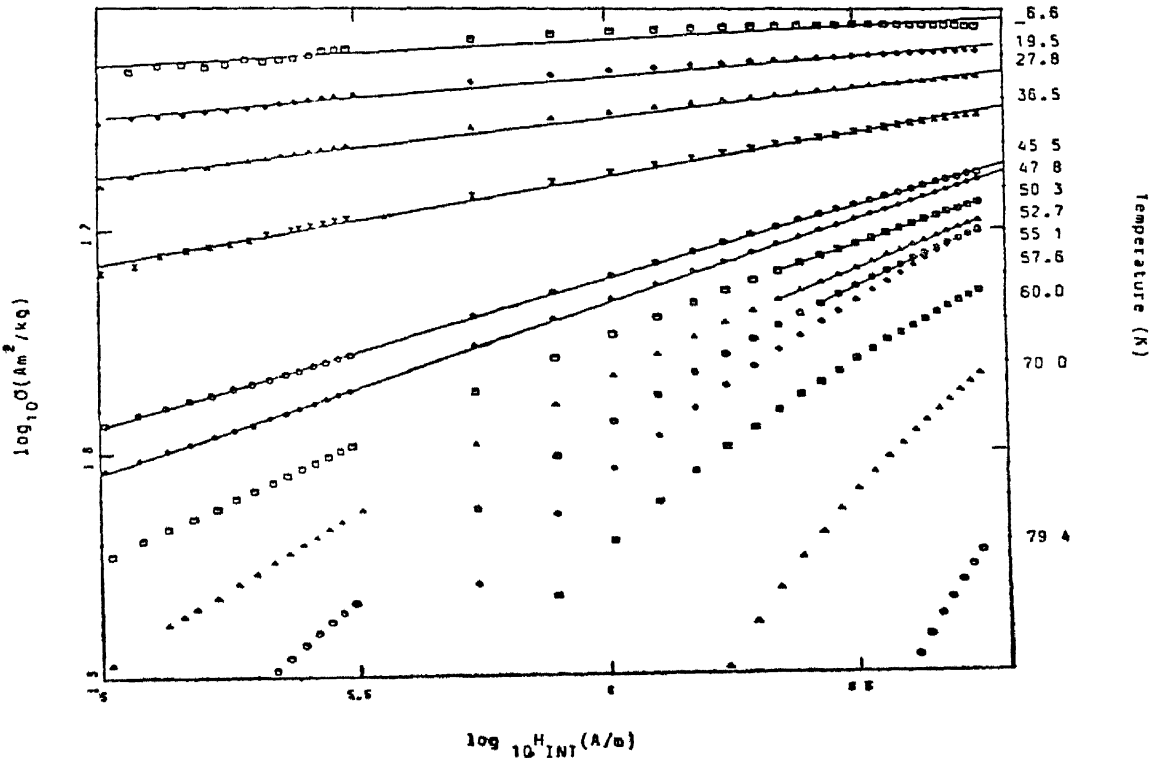


FIG 11 Magnetization isotherms of Rb_2CrCl_4 from 6 to 80 K.²⁶

theory for Rb_2CrCl_4 is being sought by neutron scattering in the critical region. Monte Carlo simulations of the scattering function $S(Q, \omega)$ for a two-dimensional XY ferromagnet suggest that the energies of the longest wavelength spin-waves should drop sharply to zero at T_c and that a central component should appear in the scattering. Both features are indeed observed²⁸ but more quantitative analysis is needed before we can be sure of their source.

Chemical variation within the $A_2\text{CrX}_4$ series makes it possible to examine how the critical properties are affected by changes in the inter-layer interactions. These may be brought about in two ways: either one can simply change the inter-layer separation, as in the $(\text{RNH}_3)_2\text{CrCl}_4$ series whose magnetic parameters are listed in Table II, or one can change the axial halide ions and hence modify the inter-layer exchange constant²⁹.

Already in Rb_2CrCl_4 the ratio of intra- to inter-layer exchange constants is 10^3 so increasing the inter-layer separation further must render the RNH_3^+ salts even better approximations to pure two-dimensional systems. The T_c 's fall as inter-layer spacing increases, but this is due in part to a drop in J . The latter is due in turn to a small puckering of the Cr-Cl layers as a result of the need to accommodate the organic sidechains and the weak hydrogen-bonds formed between the NH_3^+ and the axial and equatorial Cl^- . For example, puckering decreases the Cr-Cl-Cr angle from 180° in Rb_2CrCl_4 to 160° in $(\text{CH}_3\text{NH}_3)_2\text{CrCl}_4$.³⁰ In Fig. 12, the measured

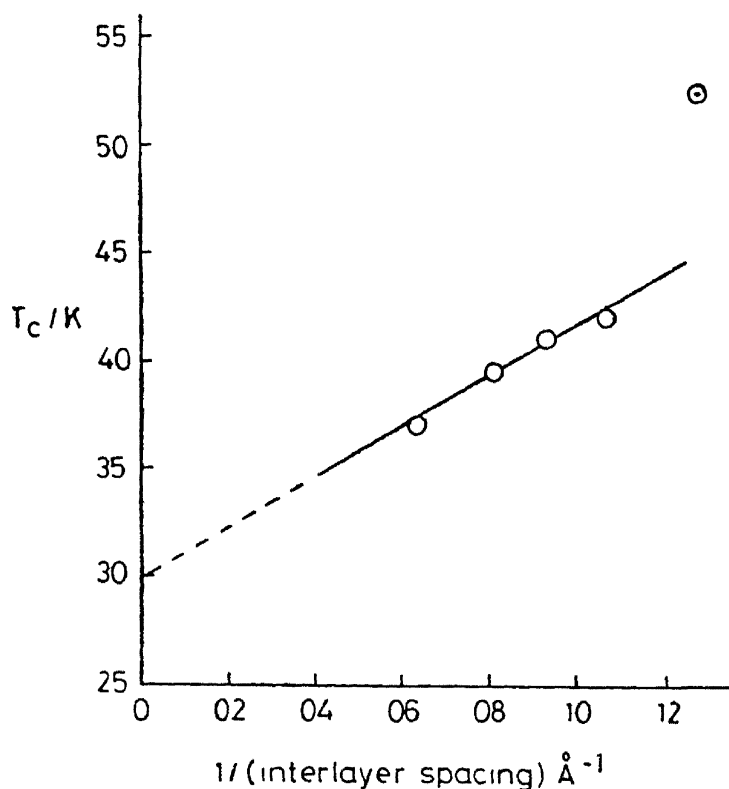


FIG 12 Curie temperatures of $A_2\text{CrCl}_4$ versus inverse interlayer separation

T_c are plotted against the reciprocal of the interlayer separation, so that an extrapolation can be made to infinite separation. T_c tends to a finite value in the region of 30K, which represents the transition temperature $T_c(2)$ of a purely two-dimensional tetrachlorochromate(II) ferromagnet. It is instructive to compare this estimate with the value predicted by the formula given by Stanley and Kaplan. These authors found that for $S \geq \frac{1}{2}$ a transition could occur in a two-dimensional Heisenberg or XY system at a finite temperature $T_c(2)$ to a state in which χ diverged but in which there was no long range order. If a small Ising-like anisotropy existed a transition to a long range ordered state would take place at a temperature $T_c \sim T_c(2)$. For a number of nearest neighbours $z = 4$ and $S = 2$ the Stanley-Kaplan formula

$$T_c(2) \sim \left(\frac{1}{10} \right) (z - 1) [2S(S + 1) - 1] \frac{J}{K} \quad .. (4)$$

predicts $T_c(2) \sim 35\text{K}$ if we take the average of the J in Table II.

As a low-dimensional magnetic system approaches the transition to a three-dimensionally ordered state from below, one anticipates a change in the spatial (d) and spin (n) dimensionality as follows

$$d \leq 3 \rightarrow d = 3$$

$$n = 3 \rightarrow n \leq 3$$

These changes should manifest themselves in a 'crossover' in the critical exponent β of the magnetization with increasing temperatures. To measure the zero-field (spontaneous) magnetization we use the intensity of magnetic elastic neutron scattering. Taking the tetrahalogenochromates as example in Rb_2CrCl_4 β changes from 0.23 to 0.33 at 0.8K below T_c ,³¹ while in $\text{Rb}_2\text{CrCl}_2\text{Br}_2$ a similar change takes place from 0.26 to 0.41 about 3K below T_c .³² The Br^- in the latter salt occupy the axial sites in the K_2NiF_4 -like structure³³ so one expects the inter-layer exchange to be stronger than in Rb_2CrCl_4 . Predicted values of β for three-dimensional Ising and Heisenberg models are 0.31 and 0.38 respectively. The values of 0.23–0.26 further below T_c are comparable to those found in other two-dimensional XY systems such as $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$ ($\beta = 0.26$)³⁴ and K_2CuF_4 ($\beta = 0.22$).

CONCLUSION

This account has concentrated on some recent examples from low-dimensional magnetism to show some of the richness and subtlety of physical phenomena that arise when interactions are confined to layers or chains within a lattice. Synthetic chemistry has brought to light many beautiful new systems, for example the transparent ferromagnets and temperature dependent helices. It has also made possible the systematic variation of parameters so that the limits of the abstract theoretical models can be probed. More surprises are undoubtedly in store, for the real world of chemistry is always more complicated than the model of theoretical physics.

ACKNOWLEDGEMENT

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ELECTRICAL TRANSPORT AND MAGNETIC PROPERTIES OF OXIDES WITH K_2NiF_4 STRUCTURE*

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A brief review of the structural features including some new results on the accommodation of oxygen non-stoichiometry is presented. The electrical transport and magnetic properties have been reviewed with the following considerations: properties of La_2BO_{4+d} ($B = Co, Ni, Cu$) and other Ln_2CuO_4 compounds, comparison of the properties of $LaSrBO_4$ compounds with that of the corresponding $LaBO_3$ compounds, influence of percolation effects.

Key Words Electrical Transport and Magnetic Properties of Oxides;
 K_2NiF_4 Structure; Percolation Effects; Three-dimensional
 Perovskites; $La_2B_4O_4$ Compounds

INTRODUCTION

A_2B_4X halides (A = alkali metal ion, B = $3d$ transition metal ion, X = halide ion) are well known to serve as magnetic model systems, especially when X is a fluoride ion and they have the K_2NiF_4 structure¹. The ionic nature of the bonding renders the $3d$ -electrons localised so that the magnetic interactions in these systems may be described by the Heisenberg Hamiltonian. Moreover, for these halides charge-balance constraints impose a formal divalent state on the B -ion so that the range of metal-halogen covalency or transfer integral is restricted. In the A_2BO_4 oxides^{2,3,4} with the K_2NiF_4 or related structures some of the constraints on the formal oxidation state of the B -ion is removed. The counter A -cations may have formal oxidation states between +1 and +3. The average oxidation state of the A -ion (typically La^{3+} and Sr^{2+}) may be varied between +2 and +3 so that the average oxidation state of the B -ions may be varied between +2 and +4. The $B-O-B$ transfer integral or the d -electron bandwidth may then be varied over a wide range so that in the limits we may have localised or itinerant (or nearly itinerant) electrons. In addition, the absence of close-packing in these systems allows strains to be accommodated so that solid solutions not normally accessible in the entire range for three-dimensional perovskite oxide systems (such as $LaAl_{1-x}Ni_xO_3$ or $LaAl_{1-x}Fe_xO_3$) may easily be prepared in the layered perovskite oxides (such as $LaSiAl_{1-x}Ni_xO_4$ and $LaSrAl_{1-x}Fe_xO_4$). The oxides with the K_2NiF_4 or related structure, therefore,

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provides unique opportunity not only to serve as model systems for magnetic interactions in low dimensions but also as model systems for the study of influence of lower dimensionality on the magnetic and electrical transport properties in transition-metal oxides

The three-dimensional perovskites ABO_3 ($B = 3d$ transition metal ion, $A = La^{3+}$, Sr^{2+} etc.) show a range of interesting properties^{2,5}. The important properties from the view-point of this article are the magnetic and electrical transport properties with special emphasis on the metal-insulator (MI) transitions⁶. Composition-controlled MI transitions in systems such as $La_{1-x}Sr_xBO_3$ ($B = Co, Mn, V$) are well known⁷. Recently, the composition-controlled MI transitions in the $LaNi_{1-x}B_xO_3$ systems ($B = Cr, Mn, Fe, Co$) have been studied.⁸ $LaNiO_3$ is metallic with a room-temperature resistivity $\sim 10^{-3}$ ohm cm and a positive temperature coefficient of resistance (TCR) at all temperatures studied so far (between 4–800 K). The $LaBO_3$ compounds are insulators. In all these systems a maximum value of the resistivity ρ_{max} ($\sim 2 \times 10^{-3}$ ohm cm) may be defined such that compositions with $\rho > \rho_{max}$ are semi-conducting in the sense that TCR is negative while these with $\rho < \rho_{max}$ are metallic with TCR being positive⁶. This value of ρ_{max} corresponds fairly closely to the value of minimum metallic conductivity σ_{min} proposed by Mott for such concentrated systems.⁹ We shall refer to σ_{min} in an experimental sense as the value of the conductivity at which TCR change sign for a composition-controlled MI transition.

In this article we shall examine the changes in the electrical transport and magnetic properties of three-dimensional perovskite oxides on reducing the dimensionality. Special attention will be paid to the systems exhibiting MI transitions in three dimensions. For a proper understanding of these studies we have discussed in brief some of the structural aspects and the electrical transport and magnetic properties of some La_2BO_4 compounds ($B = Co, Ni, Cu$). In two recent communications the aspects of crystal structure and some unusual effects of anisotropic bonding have been more extensively discussed^{4,10}.

CRYSTAL CHEMISTRY

In the A_2BO_4 oxides with the ideal tetragonal (T) K_2NiF_4 structure (Fig. 1) there is $180^\circ B-O_I-B$ interactions in the basal ab plane while along the c -axis there are $B-O_{II}-O_{II}-B$ interactions, the $B-O_{II}-O_{II}$ angle being close to 135° . Magnetic interactions along the c -axis are therefore expected to be much weaker than the interactions in the basal plane. This gives rise to the low-dimensional magnetic behaviour.

As in perovskites a tolerance factor $t (= r_{A-O}/\sqrt{2r_{B-O}})$ may be defined¹¹. The T structure has been observed in the range $1.02 \leq t \leq 0.85$ ^{11,12,4,13}. In most oxides t is considerably less than 1 and the following constraints are imposed. In the basal plane the $B-O_I-B$ distance is shortened and the $A-O_{II}-A$ distance is lengthened relative to the distance calculated from ionic radius considerations. The in-plane pressure on $B-O_I$ becomes larger as t becomes smaller. This strong

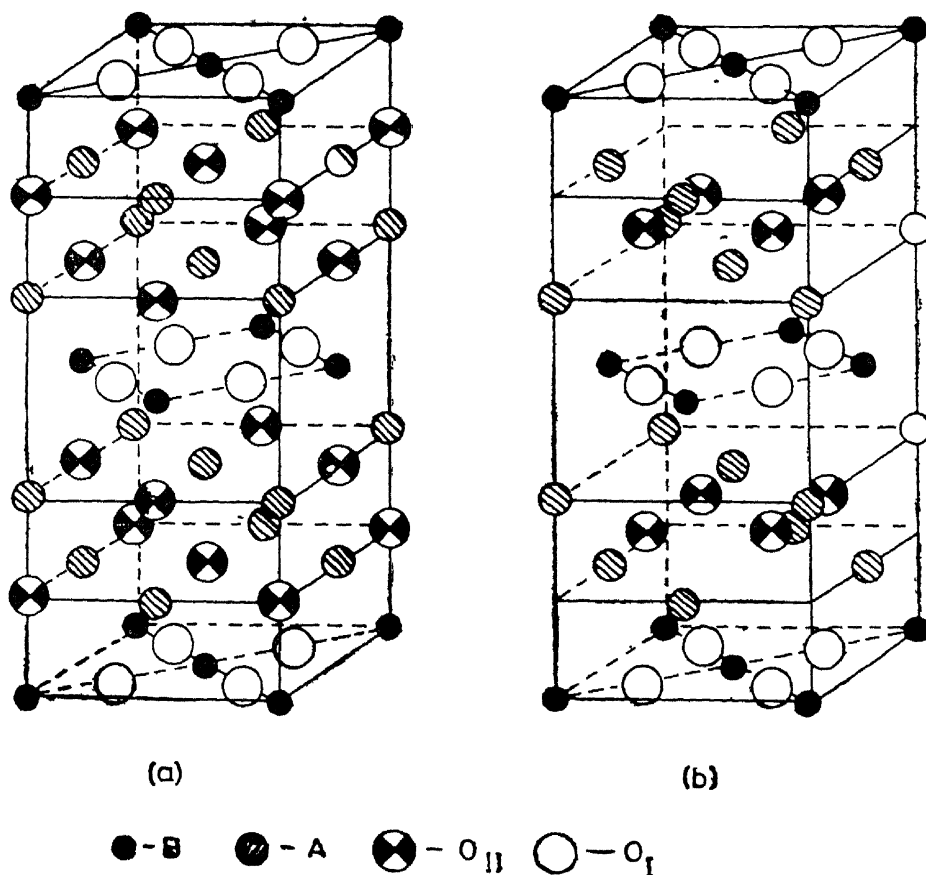


FIG 1 (a) the K_2NiF_4 (T) and (b) the T' Pr_2CuO_4 structure in A_2BO_4 oxides

internal pressure on the $B-O_I$ bond is reflected in a fairly large increase in the infrared $B-O$ stretching frequency in the layered perovskites compared to that in three-dimensional perovskites. This is especially apparent in the changes in the stretching frequency in $GdSrAlO_4$ compared to that in $GdAlO_3$.¹⁴ Such large changes are consistent with the assumption⁴ that the two-dimensional K_2NiF_4 structure imposes a rigidity to the corner-shared sheets of BO_6 octahedra. The strain due to a low tolerance factor cannot be relieved by a buckling of the octahedral network as is possible in the three-dimensional perovskite oxides.

In order to maintain the mean metal-oxygen distance the $A-O_{II}$ and $B-O_{II}$ distances along the c axis has to be adjusted. The $A-O_{II}$ distances are expected to be shortened and the $B-O_{II}$ distances to be lengthened.^{4,10} In fluorides such as K_2NiF_4 itself the tolerance factor is more than 1. The NiF_6 octahedra are accordingly compressed along the c axis. However, compounds such as Sr_4NdTaO_8 have very low tolerance factors,¹³ and unusually small c/a ratio (~ 3.00 compared to ~ 3.25 in La_2NiO_4). Thus the elongation of the BO_6 octahedra along the c axis seems to depend on the ratio of the formal oxidation states of the A and B -ions. In La_2BO_4 with trivalent A -cations and divalent B -cations, the $A-O_{II}$ interaction competes favourably with the $B-O_{II}$ interaction along the c -axis. The $A-A$ electrostatic repulsion between c -axis near-neighbours is also expected to be more

important for trivalent A -ions which will tend to shorten the $A-O_{II}$ bond. These factors could lead to short $A-O_{II}$ distances.

The importance of short $A-O_{II}$ bonds in accounting for the spectral features in the far infrared region has been stressed¹⁴. It is observed that in compounds such as La_2NiO_4 and La_2CuO_4 there is a band of considerable intensity appearing at a frequency which is much higher than that encountered in $B-O$ monoxides or in La_2O_3 . From a systematic of the changes in the frequency of this band a correlation was found with the $A-O_{II}$ distance. Hence this band was attributed to $La-O_{II}$ stretching. This was substantiated by the fact that this band is absent in compounds such as Nd_2CuO_4 in which there is no such short $Nd-O_{II}$ distances. These results and conclusions were based on studies with La_2NiO_4 which has slight oxygen excess. It is now known that stoichiometric La_2NiO_4 has a monoclinic distortion.¹⁵ Further studies are now necessary to ascertain whether the high frequency band could be due to the lower symmetry in these compounds.

One intriguing aspect of the K_2NiF_4 structure is that oxides¹⁶ such as $La_2Li_{0.5}M_{0.5}^{3+}O_4$ or $Sr_2M_{0.5}^{3+}(Nb, Ta)_{0.5}^{5+}O_4$ show no X-ray evidence for ordering of the B -cations despite fairly large charge-difference potential for such ordering.¹³ The B -cations with different charges may be looked upon as pseudo-spins with opposite orientations so that an ordering of the B -cations will be analogous to antiferromagnetic ordering. The $I4/mmm$ symmetry of the K_2NiF_4 structure imposes an inherent frustration when all the possible antiferromagnetic interactions between the spins in different layers are considered.¹⁷ The same reason may be responsible for the absence of cationic ordering in three dimensions although there be two-dimensional ordering is seen by electron-diffraction studies¹⁸ in $La_2Li_{0.5}Co_{0.5}O_4$.¹⁷ This frustration may be looked upon as an inability to convey coherently information regarding structural changes or strains in layers containing O_I ions through layers containing O_{II} ions, especially when the tolerance factor is far from the limits of stability of the tetragonal (T) structure. This may account for the stability of solid solutions such as $LaSrAl_{1-x}B_xO_4$ ($B = Ni, Fe$) for all values of x in contrast to the situation in the corresponding three-dimensional $LaAl_{1-x}B_xO_3$ compounds.

STRUCTURES RELATED TO K_2NiF_4

Several structures can result from a rearrangement of the oxygen ion positions. Three of these give rise to monoclinic distortions with $\gamma \neq 90^\circ$. Of the monoclinically distorted phases, there are two structures with $a = b$ so that the unit-cell may be indexed on the basis of an orthorhombic unit-cell. Two types of orthorhombic structures have been distinguished¹⁹⁻²¹. In the O structure the conditions for the allowed reflections are $h + k = 2n$, $k + l = 2n$, $l + h = 2n$ while for the O' structure the condition is $k + l = 2n$. The distortion to orthorhombic symmetry has been discussed in terms of two components^{4,10}. The first component involves the cooperative displacement of one half of the A and O_{II} ions along the c -axis thus reducing the $A-O_{II}$ distance and increasing the $B-O_{II}$ distance along the c -axis.

for half the A and B ions. This is the O structure proposed for Sm_2CoO_4 there being two distinguishable B (and A) cations.¹⁹ In this structure the orthorhombic b' -parameter is smaller than the a' -parameter. The second component of the orthorhombic structure involves a rotation of the BO_6 octahedra about the orthorhombic b' -axis. This leads to a decrease in the a parameter of the O' cell. The first component is not ruled out in the O' structure. The O and O' phases and their relationship have been nicely demonstrated in the system $\text{Ca}_{1+x}\text{Y}_{1-x}\text{CrO}_4$.²⁰ The temperature-dependent study on CaYCrO_4 showed that with increasing temperature the sequence is $O' \rightarrow O \rightarrow T$.

The monoclinic M structure in which $a =$ or $\neq b$ and $\gamma \neq 90^\circ$ has been reported for Pr_2NiO_4 and¹⁰ Nd_2NiO_4 and for¹⁵ stoichiometric La_2NiO_4 . An $a \neq b$ is possible only when the BO_6 octahedra are rotated about the a or b axis of the tetragonal cell. The $B\text{-O}_\Pi\text{-}B$ angle along the a or b -axis may therefore be different and this may introduce a one-dimensional component in the magnetic interactions.

There are two other structures which may be considered to be derived from the K_2NiF_4 structure. These are the T' tetragonal structures encountered in Ln_2CuO_4 compounds (Fig 1b) ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}$)^{21,23} in which the O_Π ions in the K_2NiF_4 structure having the coordinates, $0, 0, z$, are shifted to the coordinates $0.5, 0.0, 0.25$, (referred to later as O'_Π ions). In such a structure, the Ln ions have an eight-fold coordination and the Cu^{2+} ions have a four-fold coordination. A second structure derived from K_2NiF_4 are found in Ca_2CuO_3 and Sr_2CuO_3 in which half the O_Π anions (the anions on the a axis) are missing the Cu^{2+} ions again having a four-fold square-planar coordination.²²

ACCOMMODATION OF NON-STOICHIOMETRY

Oxides with the K_2NiF_4 structure are known to accommodate considerable amount of oxygen non-stoichiometry. It is now known that in $\text{La}_2\text{NiO}_{4+d}$, d can be as high as .12.^{24,25} In $\text{La}_2\text{CoO}_{4+d}$ prepared under different conditions d can be as high as .25.^{26,27} $\text{La}_{1-x}\text{Sr}_{1+x}\text{MnO}_4$ has also large oxygen excess non stoichiometry especially for small values x .²⁸ Such large oxygen excess is unusual. Drennan *et al*²⁸ have proposed that intergrowths of Ruddlesden-Popper phases such as $\text{La}_3\text{Ni}_2\text{O}_7$ and $\text{La}_4\text{Ni}_3\text{O}_{10}$ may account for the observed non-stoichiometry. However, recent resolution electron-microscope studies on powdered single crystals²⁵ as well as well-sintered air-fired ceramic samples²⁴ show that there is no intergrowth although there is considerable oxygen excess. A -site deficiencies have been suggested for lanthanum cobalt oxides to account for the oxygen excess.³⁰ Such A -site vacancies should give rise to a decrease in the density. Recent density measurement²⁷ on single crystals of $\text{La}_2\text{NiO}_{4.10}$ has shown that the density is actually higher (by about 1 per cent) than that calculated from X-ray lattice parameters. This is unusual and suggests that the excess oxygen enters the lattice as 'interstitials'. A complex polyoxygen anionic species $\text{O}_m^{-(2m-2)}$ may therefore exist. The simplest of these is the peroxide ion O_2^{2-} . Accurate X-ray studies could possibly indicate the

exact location of the excess oxygen. On examining the structure of the T and T' phases (Fig. 1) we note that for the given lattice parameters of La_2NiO_4 the distance between the O_{II} and O'_{II} ion positions is roughly 2.3 Å which is much too small for these sites to be simultaneously occupied by two oxide (O^{2-}) ions. However, this distance is sufficiently large to accommodate two oxygen atoms belonging to a peroxide-like species. It will be interesting to study whether the accommodation of excess oxygen by the formation of peroxide-like species is peculiar to the low-dimensional systems or may be found in three-dimensional systems also. More corroborative work is necessary before a peroxide-like species is to be accepted. Oxygen-deficient non-stoichiometry as in $\text{Ca}_2\text{MnO}_{4-d}$ has been attributed to the loss of O_I oxygens.³¹

La_2BO_4 COMPOUNDS

La_2NiO_4

Quite early in the literature it was noticed that the TCR of the compound with the nominal composition La_2NiO_4 changed sign around 550 K.^{32,33} This was taken as an instance of a metal-insulator transition. It was proposed that anisotropic bonding in the basal plane gives rise to a strong metal oxygen overlap in the basal plane. At low temperature the $d_{x^2-y^2}$ electrons of the Ni^{2+} ions were considered to be antiferromagnetically coupled. The so-called metal-insulator transition was then thought to be due to the breaking up of antiferromagnetic order. The gradual MI transition was attributed to the persistence of short range magnetic order at elevated temperatures in these low-dimensional systems.^{5,10} The shorter Ni— O_I distance in La_2NiO_4 ($\sim 1.93\text{Å}$) compared to that in NiO ($\sim 2.05\text{Å}$) is consistent with a strong Ni—O overlap in the former and nearly itinerant electrons in broad bands.^{5,33} The compounds with the nominal composition Pr_2NiO_4 and Nd_2NiO_4 also show similar 'metal-insulator' transition.^{10,33} These compounds have a monoclinic distortion and it was observed that the temperature at which TCR changes sign corresponds fairly closely to the temperature at which the structure becomes tetragonal.¹⁰ La_2NiO_4 itself is believed to have a superstructure indicative of lower symmetry even though X-ray diffraction may show it to have tetragonal structure.¹⁵

The anisotropic nature of electrical conduction is seen in single-crystal studies.^{15,25} A sharp decrease in the resistivity around 550 K when measured parallel to the basal plane and the absence of such a feature in the resistivity measured perpendicular to it seemed to support the early models. These studies, however, highlighted the fact that La_2NiO_4 may accommodate considerable oxygen-excess non-stoichiometry and special annealing procedures were necessary to render it stoichiometric. The properties of $\text{La}_2\text{NiO}_{4+d}$ is critically dependent on the value of d and the earlier studies lose most of their significance as far as the intrinsic properties of La_2NiO_4 is concerned as the value of d has not been specified. Recent studies seem to show that stoichiometric samples of La_2NiO_4 has a much higher resistivity than reported so far. The fairly low value of the resistivity of the air-

fired samples therefore seems to be due to excess oxygen. We have observed that samples prepared in air at 1470 K and then cooled slowly to room temperature shows a value of d close to $0.125 \pm .005$ ²⁴. Such samples show susceptibility and resistivity behaviour similar to that reported earlier.

Magnetic susceptibility studies on samples prepared in air show some unusual features. Below 200 K there is a deviation from the Curie-Weiss law which at higher temperatures gives a μ_{eff} corresponding closely to that expected for Ni^{2+} ions.³¹ Between 4 and 100 K the Curie-Weiss law is obeyed^{10,34} with no evidence for long-range magnetic ordering despite a high paramagnetic Curie temperature θ in this range. The μ_{eff} value calculated from the low-temperature region corresponds to that of an $S = \frac{1}{2}$ system. This $S = 1$ to $S = \frac{1}{2}$ transition below 200 K was attributed to antiferromagnetic coupling of the $d_{x^2-y^2}$ electrons in the basal plane. Around 200 K a change in the activation energy for electrical conduction was also observed (Fig. 2). Studies on $\text{La}_2\text{Ni}_{1-x}\text{Cu}_x\text{O}_4$ and $\text{La}_{2-2x}\text{Sr}_{2x}\text{Ni}_{1-x}\text{Ti}_x\text{O}_4$ confirmed this behaviour.¹⁰ This behaviour must now be attributed to the excess oxygen in the sample. The electrical resistivity and magnetic susceptibility behaviour is reminiscent of properties of $\text{Na}_{0.32}\text{V}_2\text{O}_5$ (Fig. 3).³⁶ It may be worth exploring how non-stoichiometry

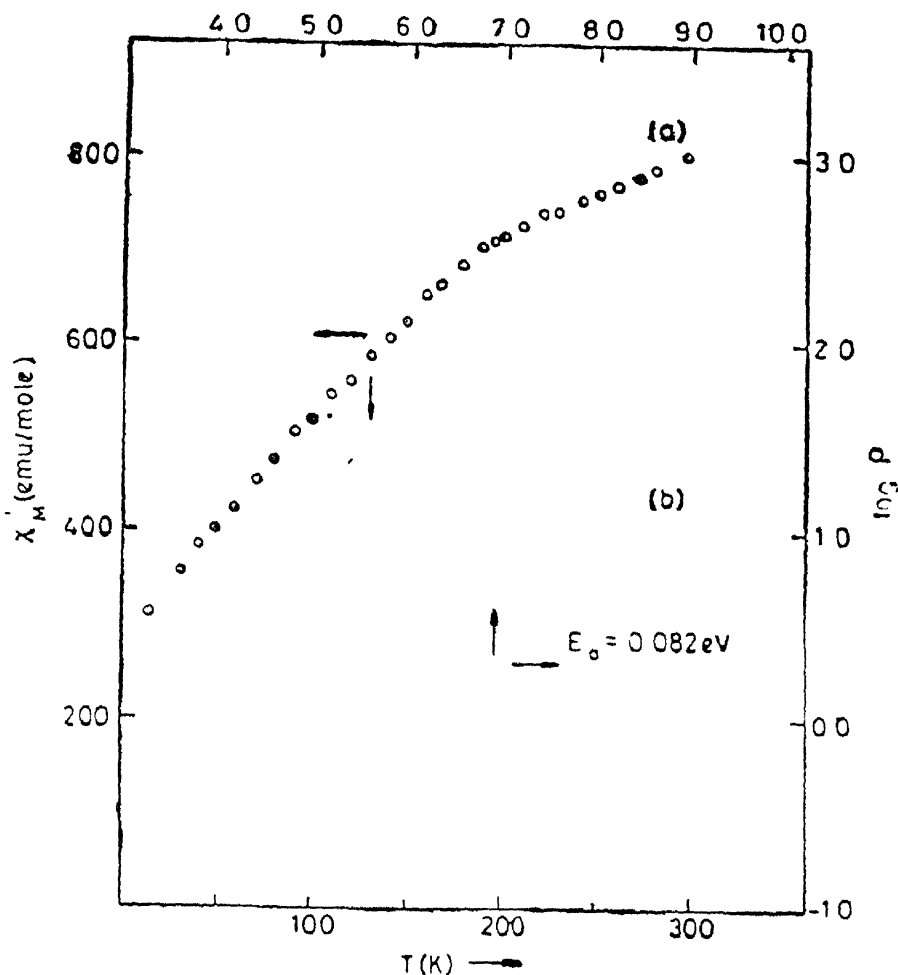


FIG. 2 χ_M^{-1} vs T and $\log \rho$ vs $1/T$ plot of an air-fired sample of La_2NiO_4 .¹⁰

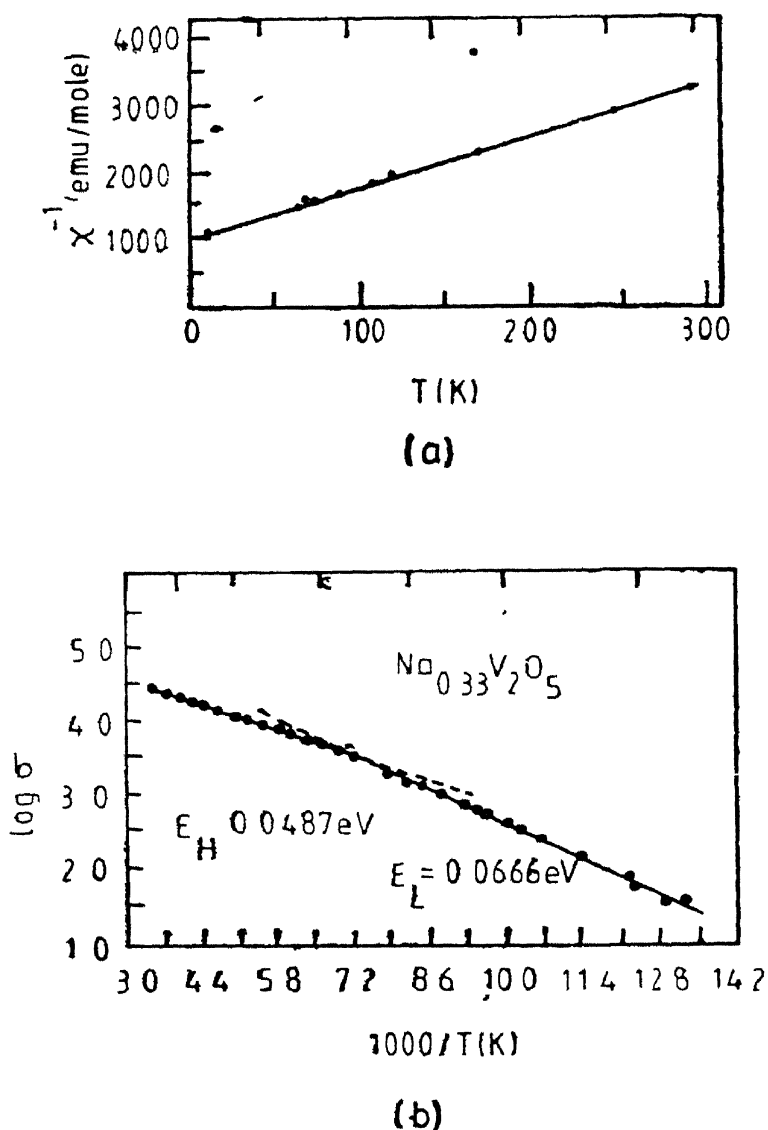


FIG 3 χ_M^{-1} vs T plot (a) and $\log \sigma$ vs $1/T$ plot of $\text{Na}_{0.33}\text{V}_2\text{O}_5$ ¹⁶

gives rise to the unusual magnetic susceptibility behaviour reminiscent of valence fluctuation systems³⁷ such as CeCu_2Si_2 . Nearly, stoichiometric samples of La_2NiO_4 have always shown so far a weak field dependence which in most samples disappears around 580 K. It is yet to be ascertained whether this is due to the presence of metallic Ni or due to canting of spins in an ordered antiferromagnet. The reduced symmetry of the stoichiometric support samples could support a Dzialoshinskii vector. Neutron diffraction studies should be helpful in resolving the problem.

It has been observed that samples close to stoichiometry show a higher resistivity than that reported for both single crystals and powders. Moreover, samples which are close to stoichiometry have a tendency to be oxidised even at low partial pressures of oxygen at moderate temperatures so that studies on such samples without a proper control of the atmosphere should be interpreted with some caution.

Despite the recent studies on the influence of non-stoichiometry much of the recent work³⁸ does not pay attention to this problem

The electrical properties of the air-fired samples as well as single crystals show some interesting features. The value of the conductivity in the so-called metallic phase in all the samples studied so far is much lower than that in other systems which exhibit metal-insulator transition or other systems which exhibit a composition-controlled MI transition.⁶ As we shall see later this may be due to the two-dimensional character. Another interesting observation is that the so-called MI transition in the air-fired samples at a temperature $T_{\min}$ at which the resistivity is a minimum may be explained by a classical diffusion equation for the conductivity of the forms $\sigma = (\sigma_0/T) \exp(-E_a/kT)$ since it is observed that $E_a \simeq kT_{\min}$.¹⁰

La_2CuO_4 and Ln_2CuO_4 ($\text{Ln} = \text{Pr}, \text{Nd}$)

La_2CuO_4 shows at high temperatures a fairly low resistivity (10^0 – 10^{-1} ohm cm)³³ The nearly temperature-independent resistivity was attributed to metallic behaviour^{5,33} However, low-temperature studies on La_2CuO_4 showed it to be semiconducting¹⁰ The Ln_2CuO_4 compounds on the other hand showed a semiconducting behaviour with a marked increase in the activation energy at high temperatures. Studies on $\text{La}_{2-x}\text{Ln}_x\text{CuO}_4$ as a function of x showed an abrupt increase in volume on going from the O structure of La_2CuO_4 to the T' structure of the Ln_2CuO_4 compounds. This is accompanied by an abrupt increase in the resistivity so that structure dominates the electrical transport properties. The large increase in the volume in the semiconducting T' phase suggests that application of

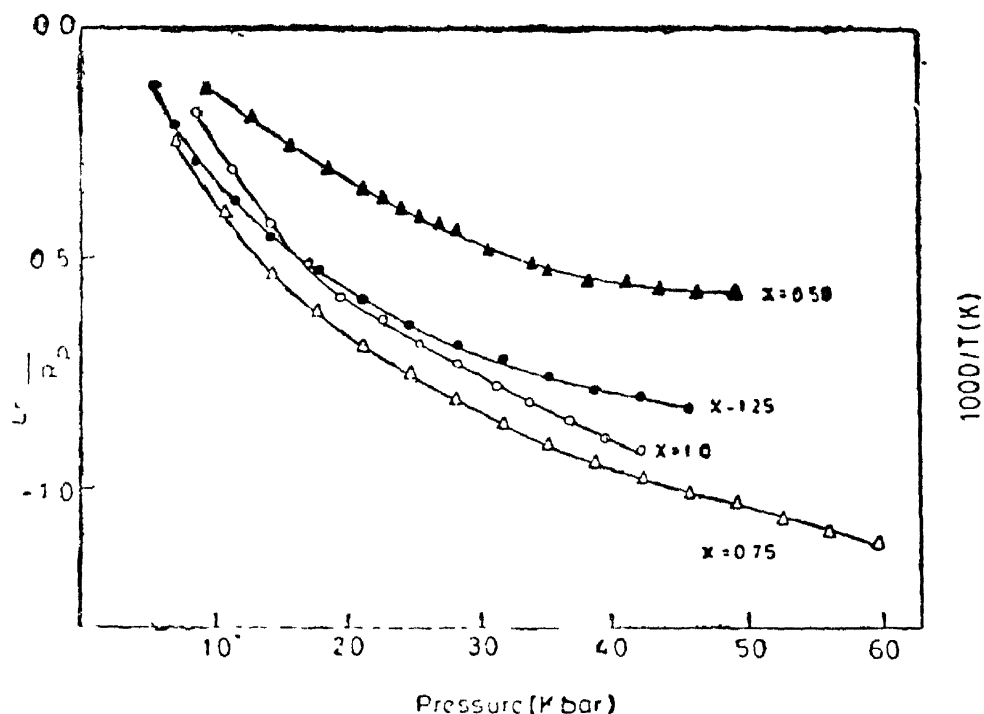


FIG 4 Variation of the resistance (R_p) of $\text{La}_{2-x}\text{Pr}_x\text{CuO}_4$ samples as a function of pressure at 300 K. R is the resistance at atmospheric pressure

pressure could induce a first-order 'semiconductor-metal' transition. This, however, was not observed²⁸ in studies upto 60kbar (Fig 4)

The low magnetic susceptibility of La_2CuO_4 has been attributed to antiferromagnetic interaction persisting at high temperature.³⁹ Interpretations based on Pauli paramagnetism is hardly convincing because of the fairly high resistivity and the low-temperature semiconducting behaviour. As we shall see later, however, there is some reason to believe that the system may be metallic as far as magnetic properties are concerned although electrical resistivity behaviour may not indicate it to be so. The susceptibility results of Singh *et al*¹⁰ has been correlated with the changes in the electrical resistivity at low temperatures (Fig 5). The number of free Cu^{2+} ions as determined from magnetic susceptibility studies starts decreasing at the temperature at which the resistivity starts increasing sharply. The magnetic susceptibility studies on Nd_2CuO_4 and Pr_2CuO_4 also showed that there is no contribution from copper ions at low temperatures indicating that there could be antiferromagnetic interactions between the copper ions.^{35,36} In this context, the break in the $\log \rho$ vs $1/T$ plots at high temperatures may be relevant as it is known that similar breaks are observed across antiferromagnetic ordering temperatures.

There may be other mechanisms by which the moments on the copper ions may be reduced. In CuO itself it is known that the moments on Cu^{2+} are reduced

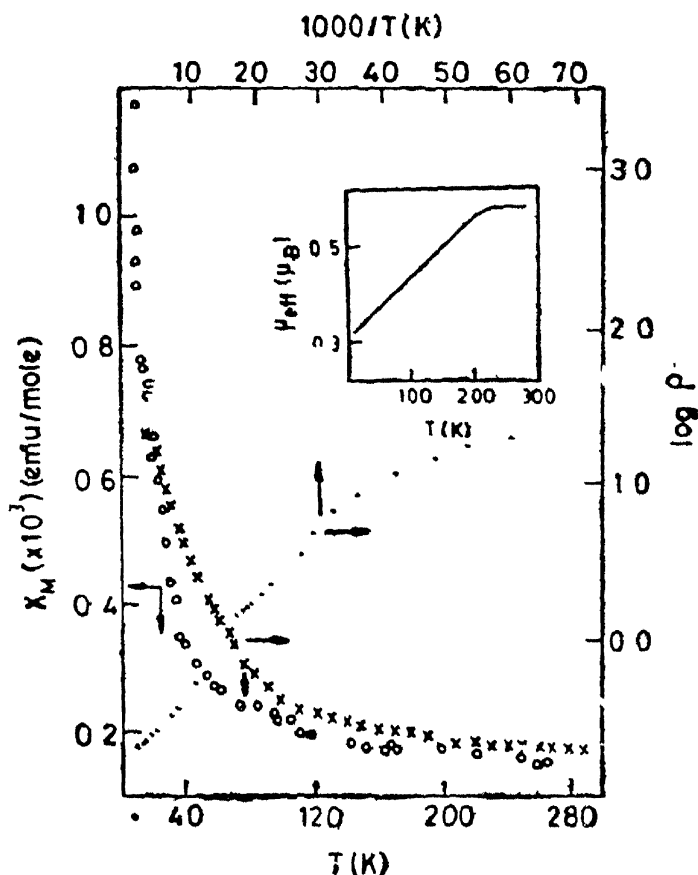


FIG 5 $\log \rho$ vs $1/T$, $\log \rho$ vs T , χ_M vs T and μ_{eff} vs T (inset) plots of La_2CuO_4 .¹⁰

although the system is insulating⁴¹ We have studied the XPS spectra of Nd_2CuO_4 and compared it to that in CuO (Fig 6) The binding energy of the $2p_{3/2}$ line is comparable to that in CuO so that the copper ions are formally in the divalent state. The satellite intensity of $2p_{3/2}$ level is much reduced in Nd_2CuO_4 compared to that in CuO . Such a reduction in the satellite intensity would indicate a marked reduction in the number of unpaired electrons on Cu^{2+} This could be attributed to:—

(i) A disproportionation of Cu^{2+} to Cu^+ and low-spin Cu^{3+} (usually stabilised in square-planar configuration) This could be dynamic or there could be a mixing of such excited configuration into the ground state tending to reduce the moments

(ii) A strong covalent Cu-O bonding with transfer of electron from oxygen to copper

Compounds such as Sr_2CuO_3 and Ca_2CuO_3 in which there are 180° Cu-O-Cu interactions also exhibit very low susceptibilities which are comparable to that of La_2CuO_4 .⁴² In the case of Ca_2CuO_3 the susceptibility decreases with decreasing temperature indicating antiferromagnetic coupling of the spins. Whether this is due to long-range antiferromagnetic coupling or dimerisation of copper pairs is not certain More interestingly, the ESR susceptibility of these compounds shows entirely different temperature independence. The ESR susceptibility in both cases increases markedly with temperature the χ_{ESR}^{-1} vs T plot showing a large ferromagnetic intercept. This behaviour is similar to that reported for TiCl_3 in which there is also one-dimensional antiferromagnetic interactions This has been attributed to end-chain effects⁴³ However, in our studies we find that at low temperatures the ESR susceptibility may be actually larger than the static susceptibility

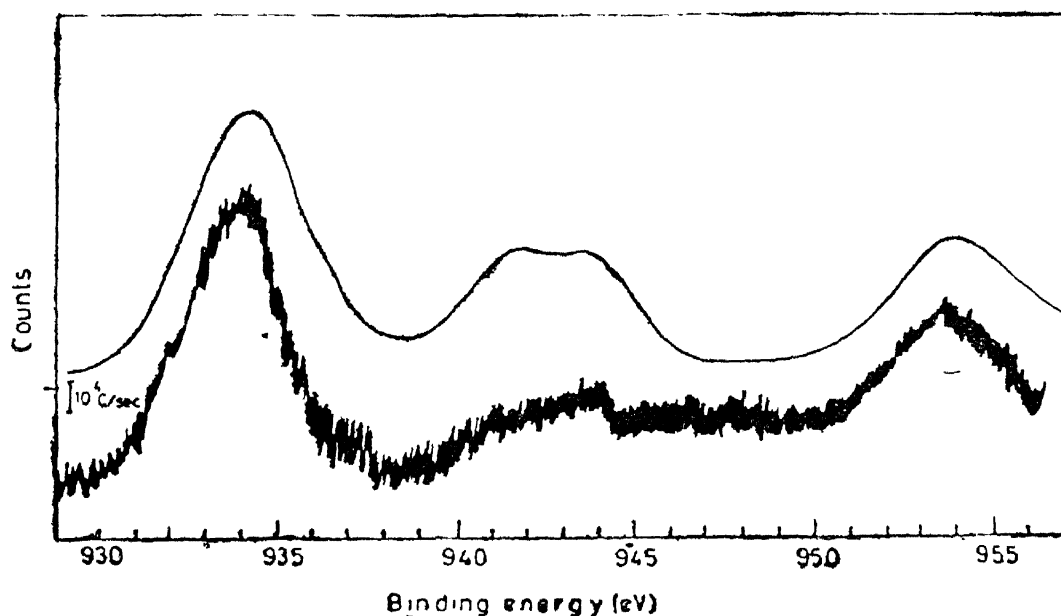


FIG 6 XPS spectra in the $\text{Cu } 2p_{3/2}$ region for CuO smooth line and Nd_2CuO_4

In La_2CuO_4 there may be other factors which could favour such a disproportionation. The tolerance factor in La_2CuO_4 is very close to the lower range of stability of the tetragonal (T) structure. A disproportionation improves the tolerance factor as the average radius of Cu^+ and Cu^{3+} is less than that of Cu^{2+} . The pseudo-tetragonal lattice parameters of La_2CuO_4 is close⁵ to that of $\text{La}_2\text{Li}_{0.5}^+\text{Cu}_{0.5}^{3+}\text{O}_4$.⁵ Since the Cu^{3+} ions are in the diamagnetic state and the Li^+ ionic radii similar to that of Cu^+ a disproportionation would not change much the lattice parameters. The orthorhombic O structure of La_2CuO_4 can also accommodate two distinguishable copper ions as mentioned earlier.

$\text{La}_2\text{CoO}_{4+d}$

The susceptibility of a $d = 0.03$ sample is shown in (Fig. 7).⁴⁸ There is clear evidence for low-dimensional magnetic ordering in terms of a broad maximum at high temperatures. In addition, there is a sharp maximum around 400 K. This feature is observed also for powdered single crystals. DSC studies on powdered single crystals as well as ceramic samples shows two transitions around 400 K. One of these is reversible with respect to temperature while the other shows a thermal hysteresis. CoO also shows a reversible transition in the DSC which is associated with antiferromagnetic ordering. The reversible DSC transition in La_2CoO_4 may therefore be associated with antiferromagnetic ordering. Neutron diffraction studies

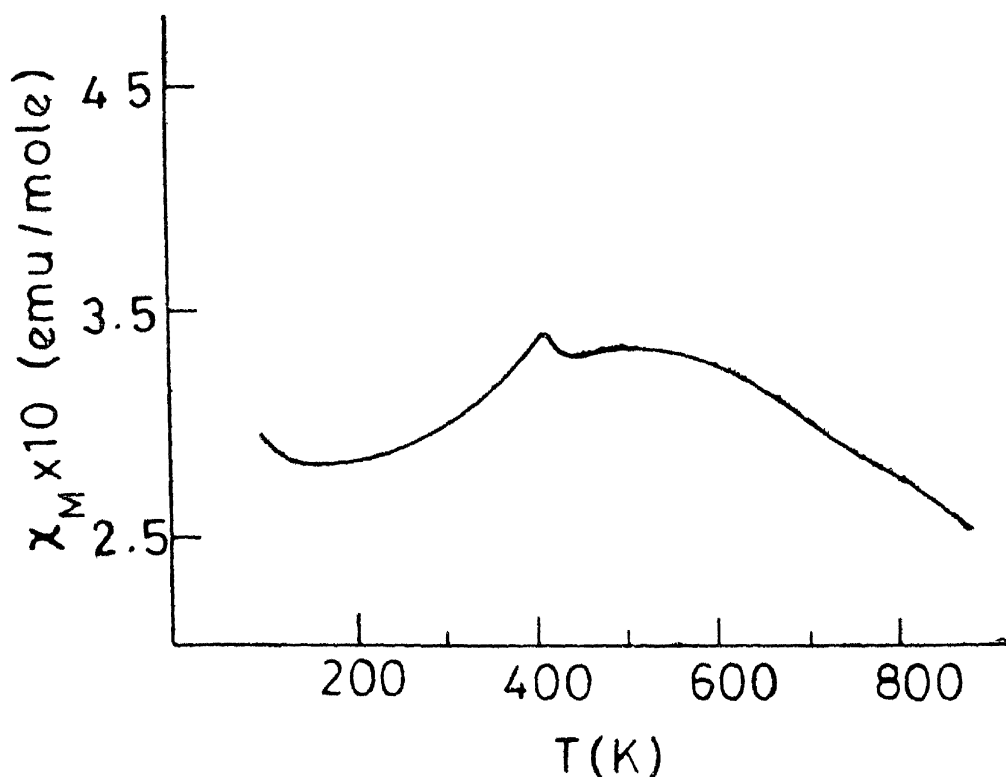


FIG 7 χ_M vs T plot of $\text{La}_2\text{CoO}_{4.03}$ ⁴⁴

or Co^{57} Mossbauer source studies would be useful in confirming the presence of antiferromagnetic interactions. Changes in d have a small but definite influence on these transitions, the transition temperature decreasing with increasing d . Just as in La_2NiO_4 stoichiometric samples of La_2CoO_4 also shows a strong field dependence in the susceptibility which persists to high temperatures.

INFLUENCE OF DIMENSIONALITY

Magnetic Properties

The three-dimensional ABO_3 perovskites and the corresponding layered perovskites ASrBO_4 (SrO ABO_3) show similar magnetic properties. In Figs. 8–10 we have compared the magnetic susceptibility behaviour of the three-dimensional perovskites LaNiO_3 , $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ and $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ with their two-dimensional analogues, respectively. We see that the magnetic susceptibilities are comparable. There is a small decrease in the paramagnetic Curie temperature for the ferromagnetic samples in two-dimensions which is consistent with their smaller nearest-neighbour spin coordination number. Similarly, LaSrFeO_4 and LaSrCrO_4 are antiferromagnet⁴⁵ just as their three-dimensional counterparts LaFeO_3 and LaCrO_3 although with reduced Neel temperatures.²

In the $\text{La}_{1-x}\text{Sr}_{1+x}\text{CoO}_4$ systems it was noticed²⁸ that the μ_{eff} values calculated from the slopes of the χ_M^{-1} vs T plots just above the Curie temperature corresponds

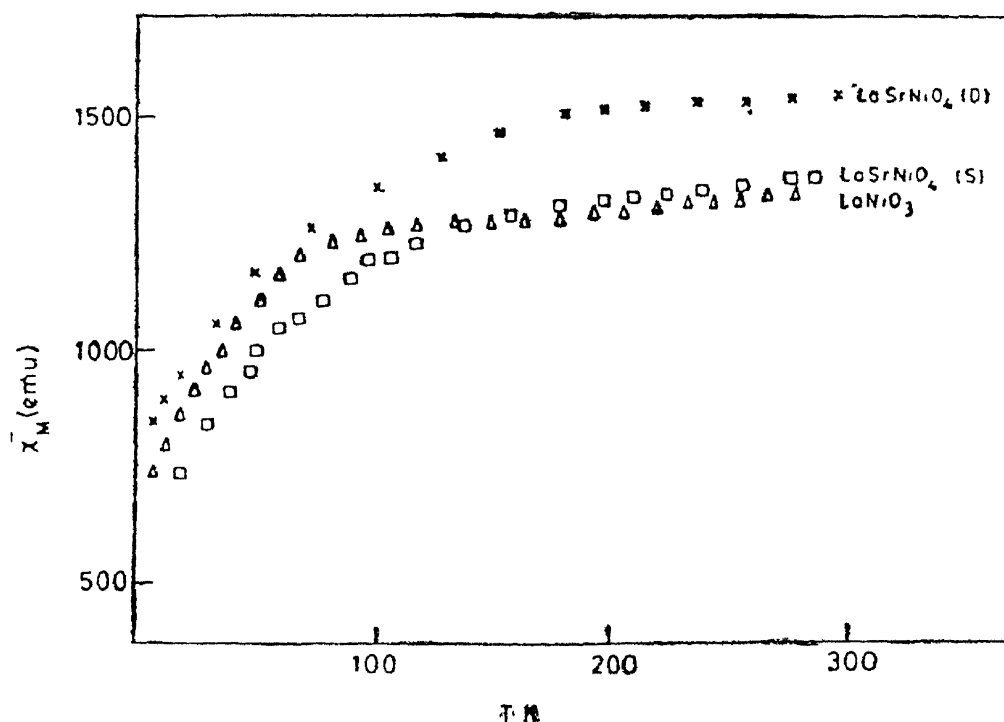


FIG 8 χ_M^{-1} vs T plots of LaNiO_3 and LaSrNiO_4 . $\text{LaSrNiO}_4(\text{S})$ is data of Mohan Ram *et al*⁴⁸ and $\text{LaSrNiO}_4(\text{D})$ is data from Demazeau *et al*

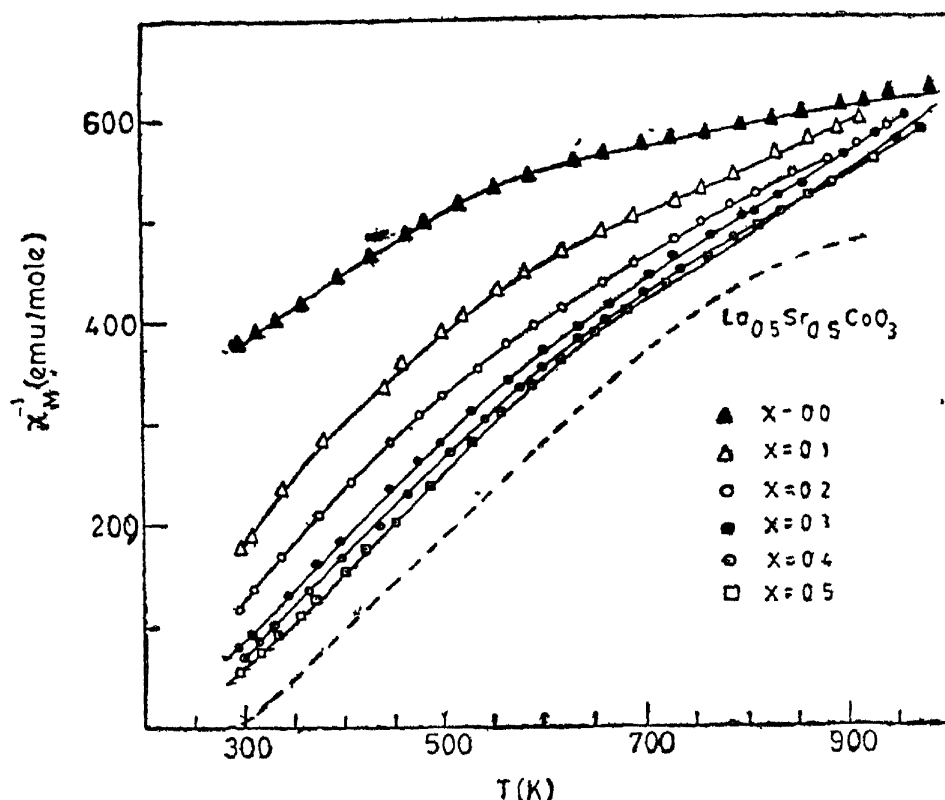


FIG 9 χ_M^{-1} vs T plots of $La_{1-x}Sr_{1+x}CoO_4$ and $La_{0.5}Sr_{0.5}CoO_3$ (dotted line).²²

to an S value of about 0.75 or an average number of 1.5 unpaired electrons. This corresponds to half the cobalt ions being in the intermediate-spin (Co^{III} , t_{2g}^5, e_g^1) state and the other half is in the low-spin tetravalent (Co^{IV} , t_{2g}^5, e_g^0) state. At higher temperatures the μ_{eff} values corresponds to the trivalent ions being in the high-spin state (Co^{3+} , t_{2g}^4, e_g^2). Similar behaviour was observed in the three dimensional systems at high temperatures. In $LaSrCoO_4$ itself magnetic susceptibility studies^{45,46} have been interpreted in terms of a low-spin to high-spin transition.

One of the surprising features in these systems is that the magnetic susceptibility of $La_{0.5}Sr_{0.5}MnO_4$ does not diverge at low temperatures despite the high paramagnetic Curie temperature (Fig 10)^{28,47,48}. There is thus no long-range ferromagnetic ordering in two-dimensional system although there is such ordering in three dimensions. Similar behaviour was observed in $LaSrMn_{0.5}Ni_{0.5}O_4$ (Fig 10)²⁸ although the three-dimensional compound is a true ferromagnet^{49,50}. On the other hand $LaSrMn_{0.5}Co_{0.5}O_4$ shows (Fig 10) a well-defined ferromagnetic ordering temperature just as²⁷ in $LaMn_{0.5}Ni_{0.5}O_3$ ²⁸. This aspect has not been explained satisfactorily. It may be interesting to see whether systems such as $LaSrMn_{0.5}Ni_{0.5}O_4$ or $La_{0.5}Sr_{1.5}MnO_4$ show metamagnetic behaviour at low temperatures.

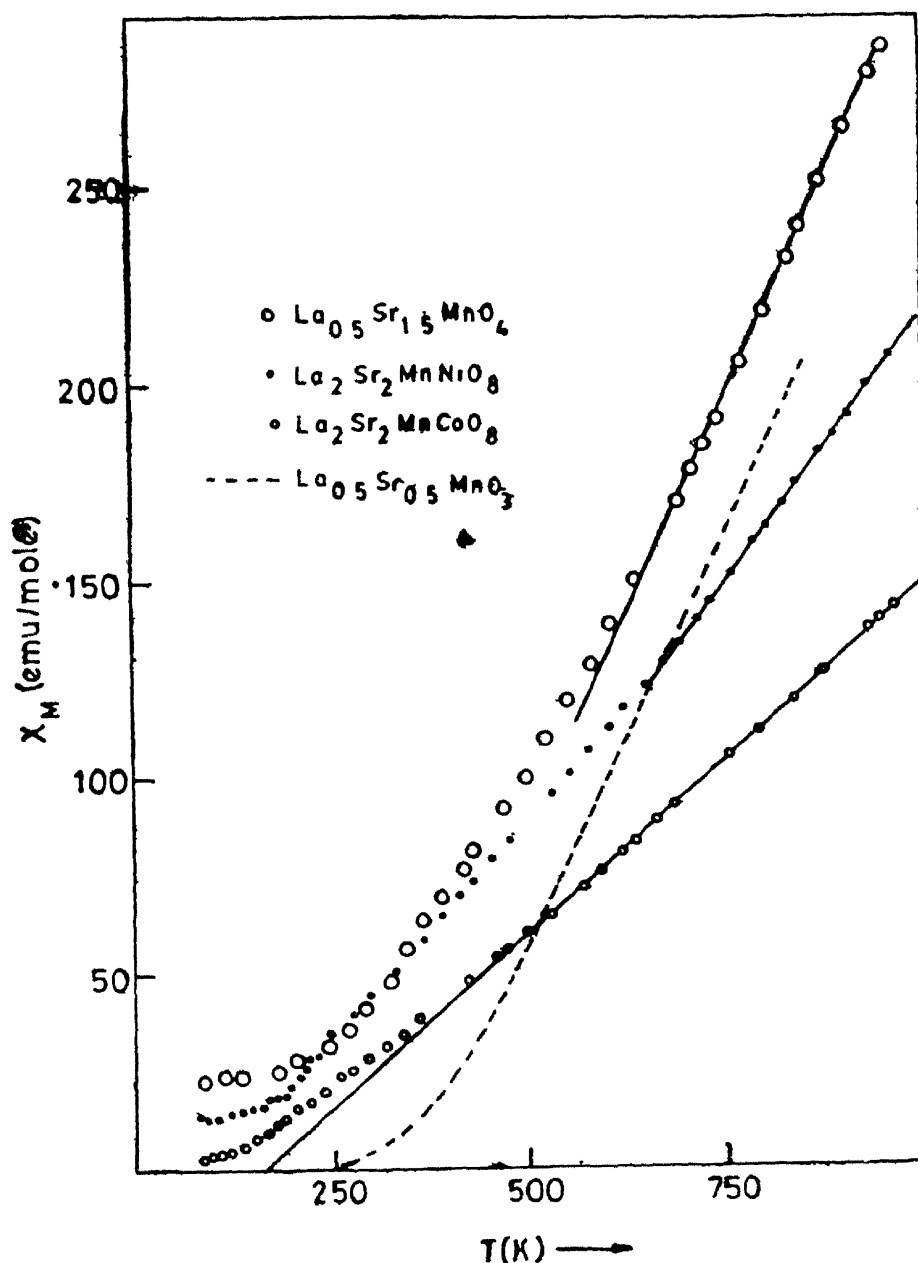


FIG 10 χ_M^{-1} vs T plots of $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$, $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4$, $\text{LaSrMn}_{0.5}\text{Ni}_{0.5}\text{O}_4$ and $\text{LaSrMn}_{0.5}\text{Co}_{0.5}\text{O}_4$ ²⁸

Electrical Transport Properties

Despite the nearly similar magnetic properties the electrical transport properties are qualitatively different as shown in Figs 11 and 12. In all the cases studied by us so far, oxides which are metallic in the three-dimensional perovskite structure are insulating in the two-dimensional structure. In the tight binding approximation, the band width is given by $2zb$, where b is the transfer integral. b determines the magnetic ordering temperature for a given spin value along with the correlation energy U for superexchange interactions. Thus the bandwidths should be marginally

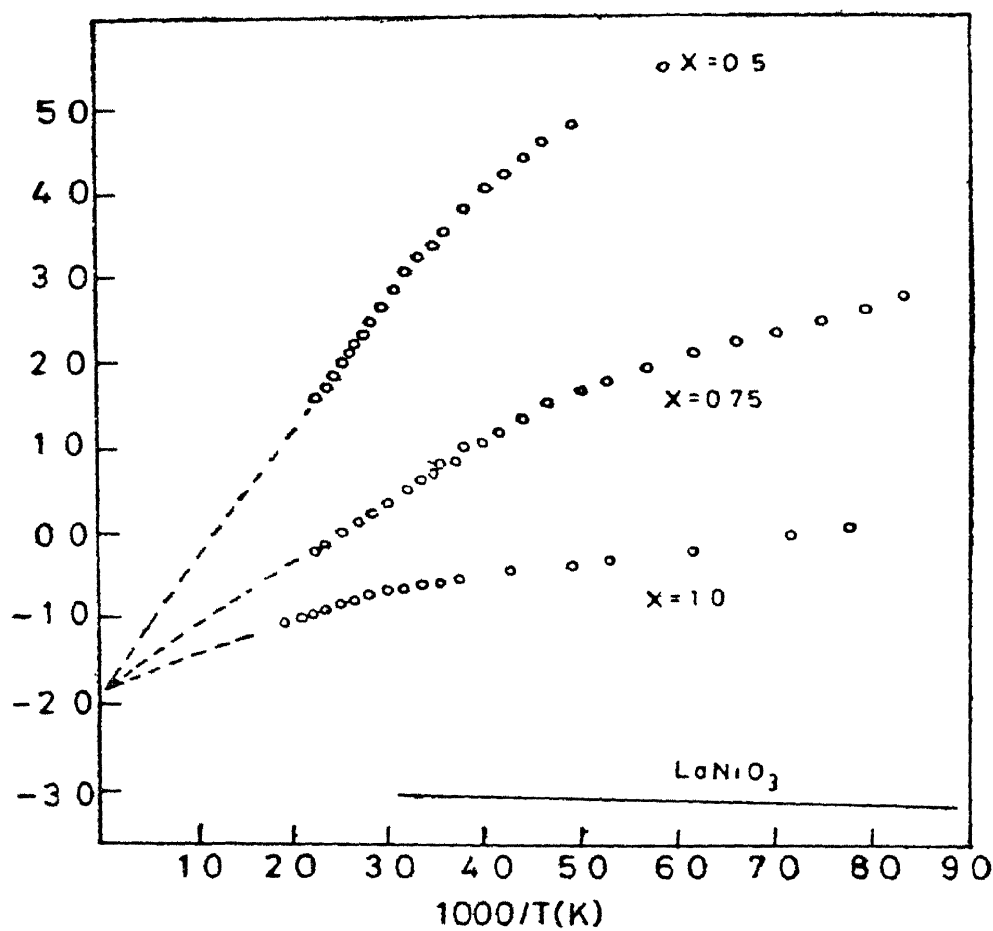


FIG 11 $\log \rho$ vs $1/T$ plot of $\text{LaSrAl}_{1-x}\text{Ni}_x\text{O}_4$ and LaNiO_3 ^{49,28}

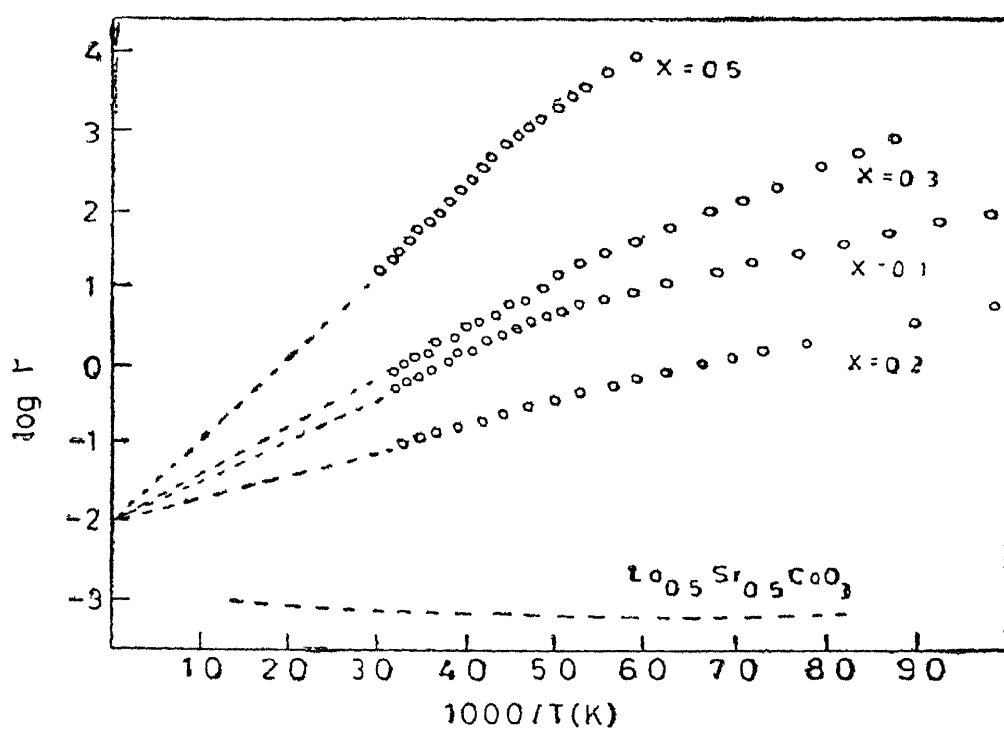


FIG 12 $\log \rho$ vs $1/T$ plots of $\text{La}_{1-x}\text{Sr}_{1+x}\text{CoO}_4$ and $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ ²⁸

smaller in the two-dimensional systems and marked changes in conductivity are not anticipated.

Seebeck coefficients do not show any changes in sign in changing dimensions. But there are some differences as far as temperature dependences are concerned. This is best illustrated in the system $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$.⁵¹ This system is considered to be an itinerant electron ferromagnet. A Zener double-exchange model was rejected on the ground that no anomalies were observed in the Seebeck effect at the magnetic ordering temperature. In the two-dimensional $\text{La}_{1-x}\text{Sr}_{1+x}\text{CoO}_4$ system clear anomalies were seen in the Seebeck effect (Fig 13) at the magnetic ordering temperature. This is most marked for the $x = 0.5$ sample. These results are consistent with a Zener double-exchange mechanism involving Co^{III} and Co^{IV} ions.

Another interesting difference is in the high-temperature intercept of the $\log \rho$ vs $1/T$ plots. In three-dimensional systems considerations based on the mobility-edge model and minimum metallic conductivity shows that the intercept in such concentrated systems should approach a value of 10^{-3} ohm cm. In most three-dimensional systems this is actually observed.^{6,52} The $\log \rho$ vs $1/T$ plots of some of the solid solutions $\text{LaSrFe}_{1-x}\text{Ni}_x\text{O}_4$ (Fig 14), $\text{La}_{1-x}\text{Sr}_{1+x}\text{CoO}_4$, $\text{LaAl}_{1-x}\text{Ni}_x\text{O}_4$

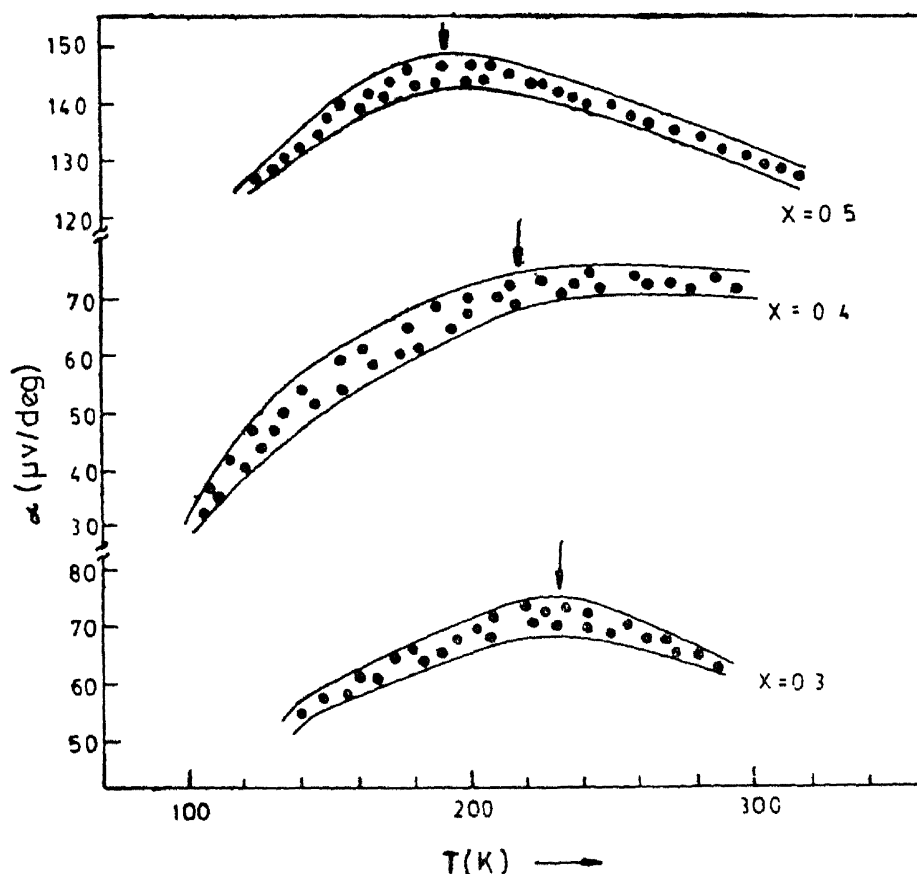


FIG 13 Variation of Seebeck coefficient with temperature for $\text{La}_{1-x}\text{Sr}_{1+x}\text{CoO}_4$. Arrows indicate magnetic ordering temperature.²⁸

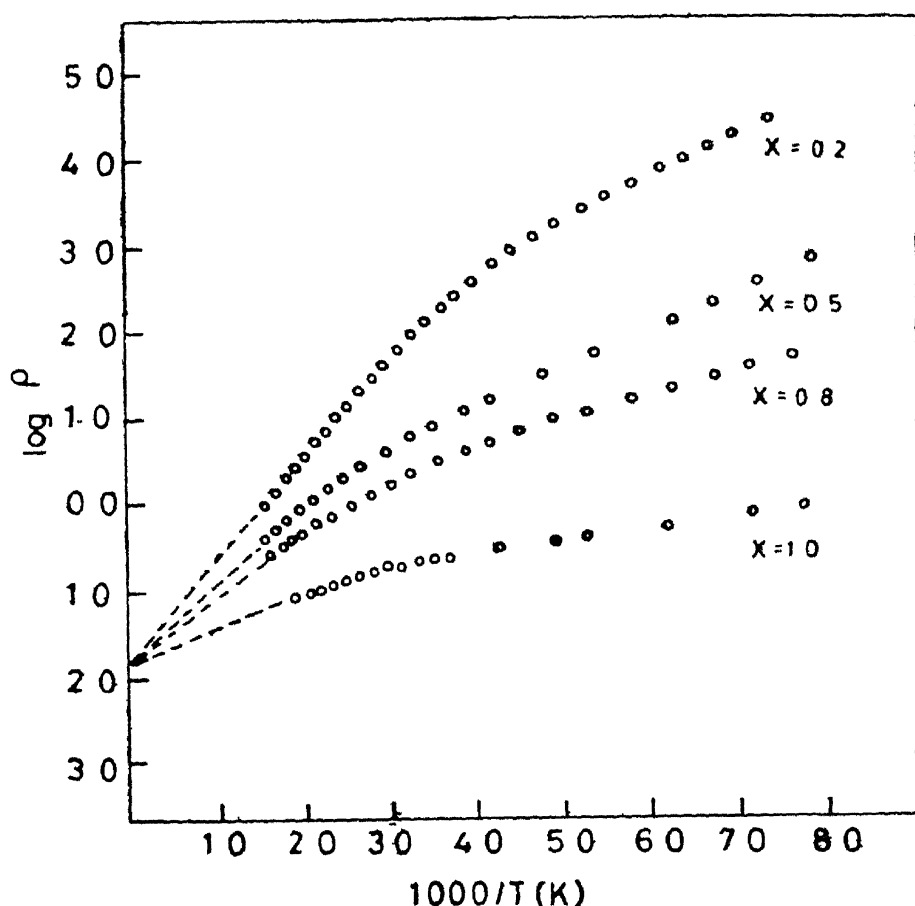


FIG. 14 $\log \rho$ vs $1/T$ plot of $\text{LaSrFe}_{1-x}\text{Ni}_x\text{O}_4$ ¹⁷

(Fig. 17) as a function of x all show an extrapolated high-temperature intercept of $\approx 10^{-2}$ ohm cm²⁸. This discrepancy is difficult to understand. This value is close to the upper limit of small-polaron conduction.⁵³ Anisotropic bonding in lower dimensions increases polaronic effects.

Among other explanations that may be put forward are the following

(i) there may be metallic conduction in the basal plane and activated conduction along the c axis. The conductivity in powdered samples may be dominated by the higher-resistivity component. Single crystal studies should resolve this problem. Anisotropy in electrical conduction of La_2NiO_4 and $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+d}$ ($x \sim 0.04$) has been observed^{15,27}. In the latter samples, preliminary studies showed that the anisotropy decreases as the conductivity was increased by increasing d . In none of these samples, however, did the resistivity in the basal plane decrease below 10^{-2} ohm cm, the limit found from high-temperature extrapolation studies.

(ii) The effects may be due to additional disorder that is introduced, for example, the Sr^{2+} ions in LaSrNiO_4 as well as the random distribution of the La^{3+} and Sr^{2+} ions. This effect may not be important in the $\text{La}_{0.5}\text{Sr}_{1.5}\text{BO}_4$ systems. It is interesting to note that BaPbO_3 is metallic while Ba_2PbO_4 is an insulator.

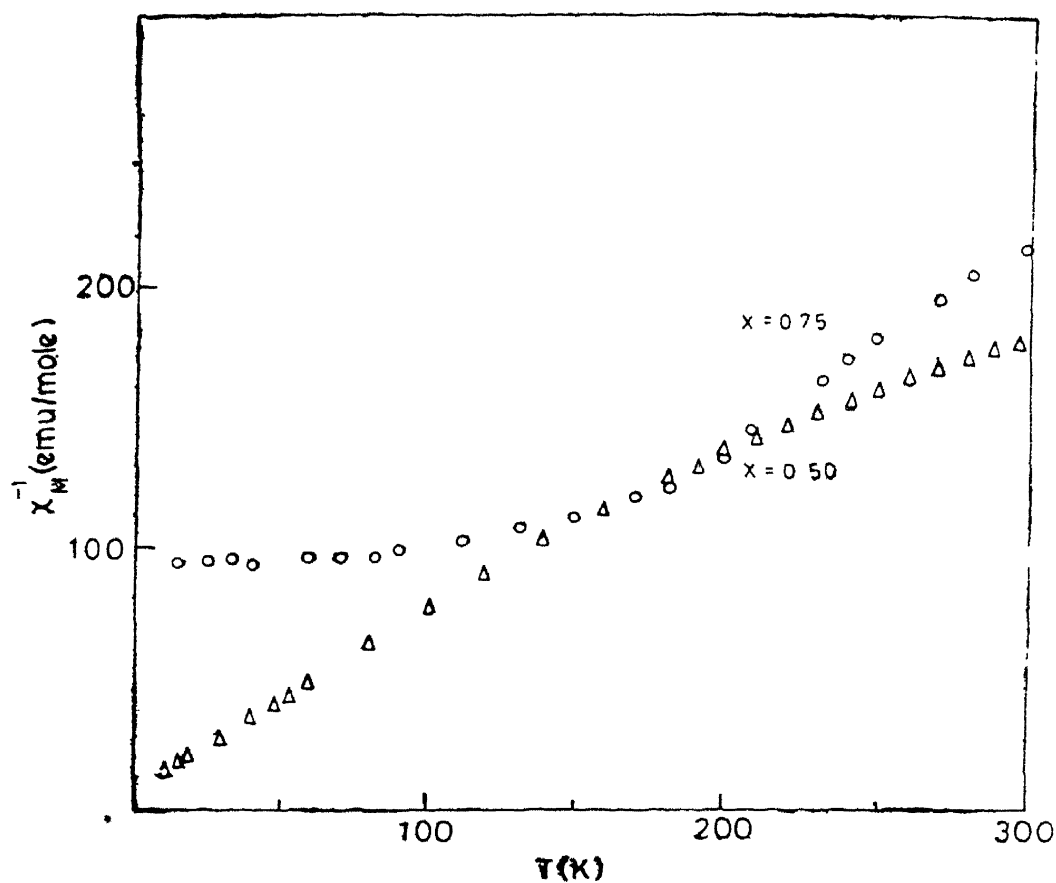
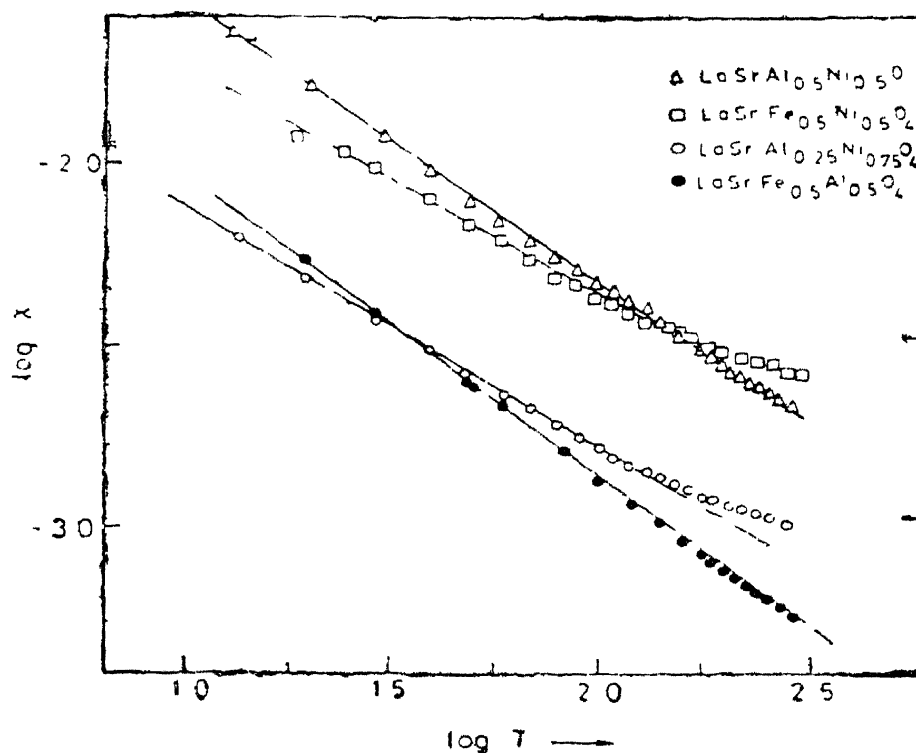
Comparisons with metallic SrBO_3 compounds and the corresponding Sr_2BO_4 compounds should be useful.

(iii) We may adopt the suggestion made among others by Mott and Davies⁵⁶ that polaronic effects decrease the bandwidth without affecting the transfer integral mainly responsible for magnetic interactions. The increase in the metal-oxygen stretching frequency observed in the K_2NiF_4 structures suggests that polaronic effects are stronger. Since compounds such as LaNiO_3 and $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ have conductivities close to the minimum metallic conductivity, decrease in bandwidth may easily render these systems insulating. In this context, it may be remarked that since almost all oxides undergoing a temperature-induced metal-insulator transition have a low-dimensional character in the insulating phase, and in the metallic phase have conductivity close to $\sigma_{\min}$, such transition may be controlled by changes in the dimensionality of electrical conduction and is dominated by polaronic effects.

In order to explore the effects of dimensionality further, we have studied the changes in the electrical transport properties of perovskites in the homologous series $(\text{LaO})_n(\text{LaNiO}_3)_n$. In these systems the number of perovskite-like layers is n . These studies²³ showed clearly a gradual increase in the conductivity as n was increased. Although the results show a striking dependence on n the choice of the system is unfortunate as there is a change in the number of Ni^{3+} ions. The increase in conductivity with n , however, cannot simply be attributed to the Ni^{3+} content as LaSrNiO_4 has a high resistivity. These results seem to imply that $\sigma_{\min}$ increases as the three-dimensional character of the system increases which is consistent with an earlier observations on the value of the high-temperature intercept for the oxides with the K_2NiF_4 structure. Another important feature that emerged from these studies is that the magnetic susceptibility per gram atom of Ni is nearly independent of n although there is large changes in resistivity. LaSrNiO_4 and LaNiO_3 also show similar magnetic susceptibility behaviour despite large differences in resistivity.

PERCOLATION EFFECTS

It has been demonstrated in studies⁵⁴ with fluorides such as $\text{K}_2\text{Mg}_{1-x}\text{Mn}_x\text{F}_4$ that Neel temperature drops abruptly to zero when the value of x decreases below the site-percolation threshold value of ~ 0.60 implying that nearest neighbour interactions determine the ordering temperature. In the $\text{LaSrAl}_{1-x}\text{Fe}_x\text{O}_4$ system, the $x = 0.75$ composition showed evidence for long-range order while the $x = 0.5$ sample did not show such evidence down to 12K (Fig. 15). In the three-dimensional system $\text{LaAl}_{1-x}\text{Fe}_x\text{O}_3$ the $x = 0.5$ composition showed both Mossbauer and magnetic susceptibility evidence for the existence of long-range antiferromagnetic order. In the $\text{LaSrAl}_{1-x}\text{Ni}_x\text{O}_4$ system the magnetic susceptibility per g atom of Ni decreases sharply on going from $x = 0.5$ to 0.75. It seems therefore that these effects could also be attributed to percolation. The $\log \chi$ vs $\log T$ plots in these systems (Fig. 16) was fairly linear over large temperature ranges. The slopes

FIG 15 $\log \chi_M$ vs $\log T$ plots of some samples.FIG 16 χ_M^{-1} vs T plot of $\text{LaSrAl}_{1-x}\text{Fe}_x\text{O}_4$ $x = 0.75$ and 0.5

were less than 1 implying that the susceptibility obeyed the relation $\chi = C/T^\beta$, where β is less than 1. This kind of behaviour is seen in amorphous antiferromagnets⁵⁵ The behaviour in the oxides may then be attributed to the presence of isolated clusters of different sizes within which the spins are antiferromagnetically coupled. These clusters behave like superparamagnetic particles of different spins. The magnitude of the exchange energy between these clusters would therefore be different. The hierarchy of exchange strengths may give rise to the $T^{-\beta}$ dependence observed at low temperatures for the susceptibility. At the lowest temperatures three-dimensional effects may dominate although this has not been seen in our studies.

In the $\text{LaSrNi}_{1-x}\text{Fe}_x\text{O}_4$ system (Fig. 17) it is observed that the magnetic ordering temperature decreases much faster than in the $\text{LaSrAl}_{1-x}\text{Fe}_x\text{O}_4$ system as

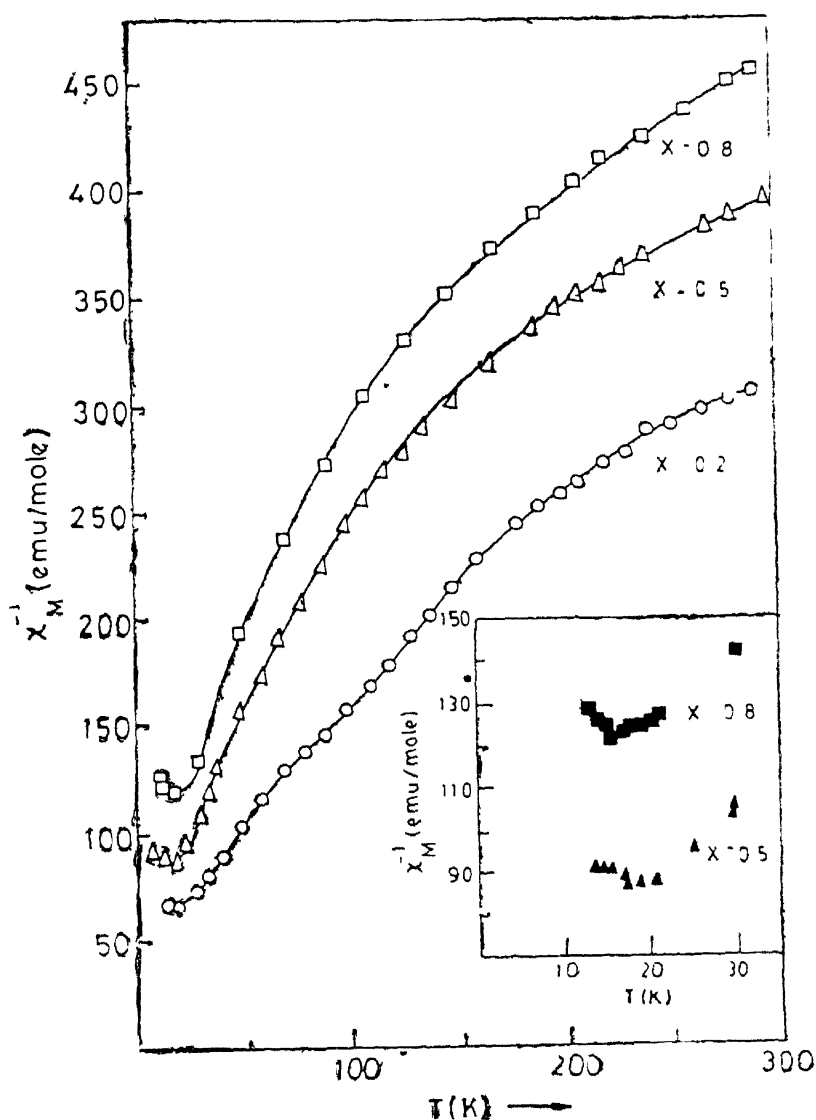


FIG 17 χ_M^{-1} vs T plot of $\text{LaSrFe}_{1-x}\text{Ni}_x\text{O}_4$ samples²⁸

seen by a comparison of Figs 24 and 23 of Ref 28. Apparently, even when x is above the percolation threshold, the Ni ions involve the Fe ions on the periphery of the Fe clusters interactions which oppose the magnetic ordering. Frustration may occur for example if the Ni-Fe interactions are ferromagnetic and the Ni-O-Ni interactions antiferromagnetic. This effectively decreases the concentration of Fe ions in the core of the clusters which are not involved in frustrated interactions. At the lowest temperatures the decrease in the susceptibility (Fig. 17) must be attributed to antiferromagnetic ordering of these clusters. This should be dominated by the strength of the Ni-O-Ni interactions. Similar behaviour is observed in the $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_3$ systems.

Since in these transition metal oxides the magnetic as well as the electrical properties are dominated by the d -electrons, one may expect percolation effects appearing in electrical transport properties as well. We have failed to observe such effects in electrical resistivity studies. However, the sign of the Seebeck coefficient at room temperature shows some correlation. Thus in the $\text{LaM}_{1-x}\text{Ni}_x\text{O}_3$ system ($M = \text{Cr, Fe, Co, Mn}$) the sign of the Seebeck coefficient changes sign from positive to negative when x becomes greater than ~ 0.3 which is the site percolation threshold for a cubic system. In $\text{LaSrAl}_{1-x}\text{Ni}_x\text{O}_4$ and $\text{LaSrFe}_{1-x}\text{Ni}_x\text{O}_4$ such a change in the room-temperature Seebeck coefficient occurs when $x \sim 0.60$. It is interesting to note that in several $\text{La}_{1-x}\text{Sr}_x\text{MO}_3$ systems ($M = \text{Co, V, Mn}$) the metal-insulator transition is observed when $x = 0.28 \pm 0.02$ which is close to the site-percolation threshold value for three-dimensional systems⁶. We note that in these three-dimensional systems the $0.70 < x < 0.30$ compositions have connected paths of both trivalent and tetravalent ions. Such a situation is not possible in the two-dimensional systems. Whether this has a role to play in explaining some of the anomalous properties has yet to be examined.

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SOL-GEL ROUTE TO INORGANIC MATERIAL SYNTHESIS

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The sol-gel process has added a new degree of freedom to the synthesis of various materials e.g., glasses, glass-ceramics and oxides of practical importance. This paper reviews the present state of understanding with regard to the mechanisms involved in the gel formation and densification on specific heat-treatments. The wide range of materials prepared by this technique are delineated and some of its future possibilities are discussed.

Key Words . Sol-Gel Process; Inorganic Material Synthesis; Glass Ceramics; Glasses.

INTRODUCTION

SOL-GEL method of preparing materials has emerged as a powerful technique in recent years.¹ Initially, the interest in classical gel-derived materials arose from some of their special characteristics viz., submicron particle size leading to high reactivity and low processing temperatures, high purity and homogeneity attainable in multi-component systems.²⁻⁵ Lately, the advantages of sol-gel process have been exploited in making a wide range of materials especially, glasses, glass-ceramics and oxides of practical importance.⁶⁻⁸ In this paper, we give an overview of the subject emphasizing on the current understanding of the mechanisms of gel formation and their subsequent conversion to the desired products by suitable heat treatment.

SOL-GEL MECHANISM

A sol represents a suspension or dispersion of discrete colloidal particles, while gels are colloidal solids usually containing also a fluid component and having a network internal structure so that both the solid and the fluid components are in a highly dispersed state. Gel is a broad term⁹ covering both liquid-rich and liquid-free systems. The term xerogel is used to designate dry gels, e.g. a sheet of gelatin, a foil of cellophane etc.

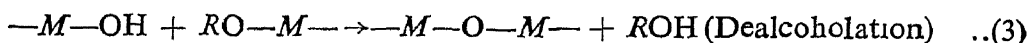
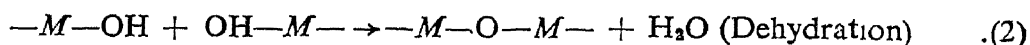
Gelation

Gelation, the setting of colloidal solutions, can proceed by different routes⁹ to produce either colloidal or polymeric gels.¹⁰ In colloidal gels, electrolytic or steric effects in the precursor solution or sol dominate gel formation, while for polymeric gels, the relative rates and extents of chemical reactions (including polymerization) are critical. In organic systems, the gel consists of polymers or long chain molecules crosslinked to create a tangled network which extends through

a liquid, whereas, the so-called colloidal gels consist of discrete colloidal particles which are linked together into branched chains which form extensive networks throughout the liquid medium by a mechanism similar to flocculation (hydrogen bond, electrostatic attraction)¹¹ By controlling the pH, dilution, and water content of the solutions, polymeric or colloidal gels can be obtained¹⁰ At low pH (< 2.5) in alkoxide solutions with low water to alkoxide molar ratios, relatively linear polymeric species are produced, which can crosslink to yield a polymeric gel. At higher pH values (> 2.5), regardless of the water content, alkoxides and polysilicic acids polymerize to form colloidal silica or weakly crosslinked clusters

Polymeric Gels—The most widely used starting materials for making polymeric oxide gels are metal alkoxides. These compounds have the general formula $M(OR)_n$, where M is a metal ion and R is an alkyl group. There are essentially four steps involved in the process of formation of a polymeric gel. These are as follows;

- (a) Reaction of several metal or nonmetal alkoxides
 (b) Hydrolysis $M(OR)_n + xH_2O \rightarrow M(OH)_x(OR)_{n-x} + xROH$
 (c) Polycondensation



It is to be noted that all the above reactions take place simultaneously¹² Gel state can be achieved in two ways¹ In the first case, removal of the solvent forms

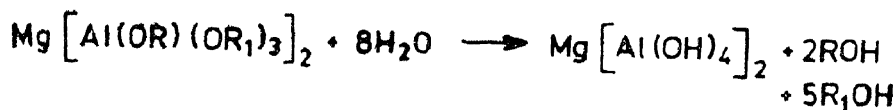
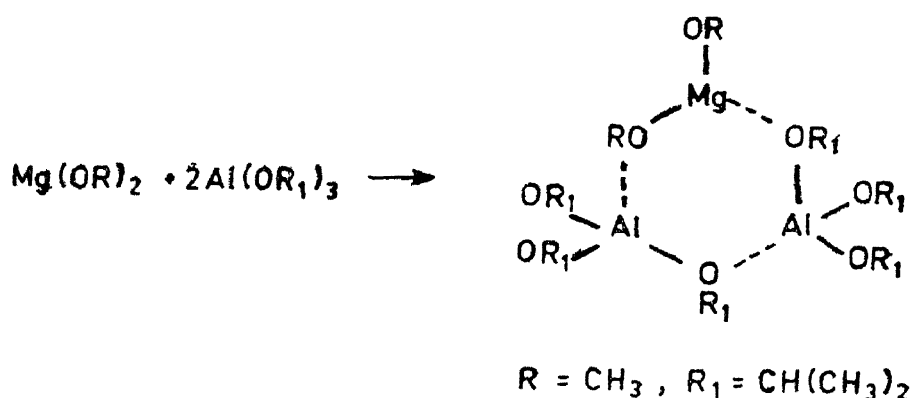


FIG 1 Spinel synthesis via alkoxide route⁷

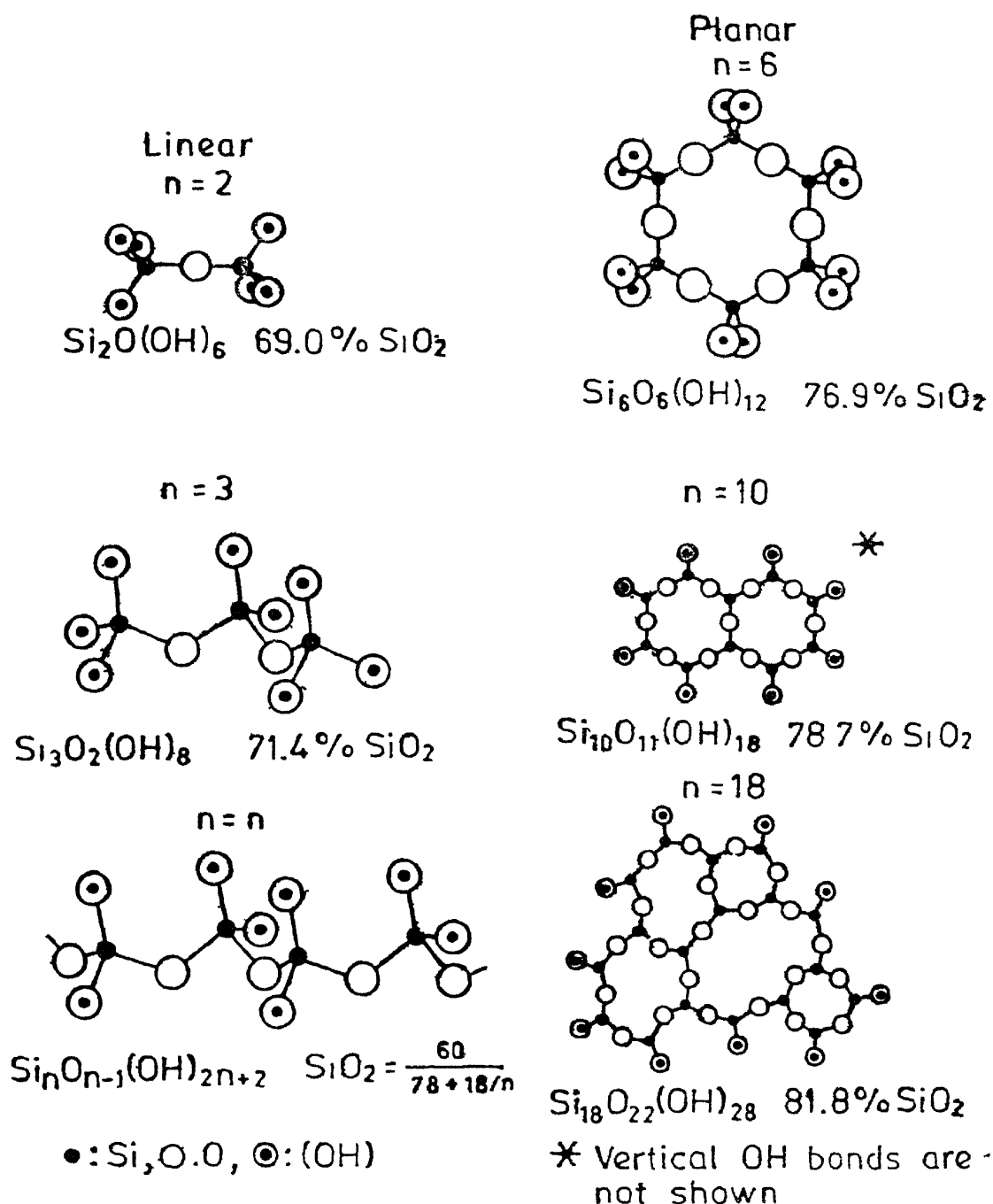


FIG 2 Example of how molecular size and polymerization type affect chemical make-up of silanol polymers¹⁴

the polymer species into closer proximity, thereby increasing the probability of crosslinking between them. When sufficient crosslinking is achieved, the viscosity of the solution increases rapidly and the solution gels. In the second case, aging of the solution allows the dehydration and hydrolysis reaction to proceed whenever polymer species randomly collide in solution. Continued polymerization leads to network formation, expulsion of organic groups, and gelation. Several solution parameters must be considered to ensure success in obtaining polymeric gels. The

important parameters are molar ratio of water to alkoxide, pH of the solution (Acid or base can act as a catalyst)¹³ and temperature. Fig. 1 gives a typical example of spinel synthesis by the alkoxide route⁷ and Fig 2 depicts the chemical make up of Silanol ($-\text{SiOH}$) polymers of different sizes made by a similar reaction¹⁴

Colloidal Gels—Colloidal gels are typically formed from metallic salt solution (Chlorides, nitrates, sulfates etc) and oxide or hydroxide sols. The presence of potential determining ions (H^+ or OH^- for oxide/hydroxide systems) as well as nonpotential determining ions affect the stability of the colloids through their effect on double layer.¹⁵ According to Dell,¹⁶ there are three principal methods to form a gel from concentrated sols, (a) removal of water; (b) neutralization of the stabilizing anion, and (c) removal of acid by solvent extraction. Yoldas¹⁷ used both dehydration and neutralization (using ammonia) to gel boehmite (hydrous aluminium oxide) sols. Gelation by extraction of acid has been discussed by Dell,¹⁶ who noted that the technique had been applied to many ceramic systems including calcia stabilized zirconia, manganese zinc ferrite, strontium ferrite, yttrium iron granet and lead zirconium titanate. Marboe and Bentur¹⁸ have discussed the effects of precipitation and aging conditions on the formation of gels (aluminium hydroxide gels). When this material is precipitated from cold acidic solutions by rapid addition of base, an amorphous gelatinous solid is formed upon dehydration, the solid often forms aluminium trihydrate $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, but under suitable aging conditions bayerite $\text{Al}(\text{OH})_3$ is formed. If aluminium hydroxide is formed by very slow addition of base to a hot aqueous solution of an aluminium salt, the resulting amorphous gel ages to form boehmite $\text{AlO}(\text{OH})$. The pH of the solution also plays an important role here. When $\text{Al}(\text{NO}_3)_3$ is decomposed to the hydroxide by base addition at $\text{pH} = 10$, aging for 600hr develops microcrystalline $\text{Al}(\text{OH})_3$, but precipitation at $\text{pH} = 5$ yields gels which retain their amorphous character even after 6 days. The effects of temperature in case of aluminium hydroxides system have been studied by Yoldas.¹⁹ For gels formed by hydrolysis of aluminium sec-butoxide and aluminium isopropoxide at 20°C , the precipitate consists largely of amorphous monohydroxide, while the same process performed at 80°C produces boehmite.

Aging and Desiccation

The effect of volume changes on stresses produced during drying has been discussed by Cooper²⁰. The permissible drying rates, consistent with the avoidance of fracture, were evaluated and found to vary inversely with the thickness of the body being dried. Changes in gel structure during aging and desiccation were studied by Zarzycki *et al*²¹. During the initial stages of drying, the volume change of the gel is equal to the volume of evaporated liquid. The gel network is still flexible and can rearrange to accommodate the decreasing volume. All pores are filled with solvent and liquid-air interfaces are not present. As drying proceeds, the gel network becomes more restricted, and the removal of liquid leads to the formation of such interfaces and the development of capillary stresses. The tendency toward fragmentation due to capillary stress is determined by both the average pore size and the pore size distribution. The larger the diameter of the pores, the lower

is the capillary pressure and at the same time minimum in pore size variations gives rise to minimum pressure differences between the capillaries with consequent lowering of stresses. An example is provided by the work of Yoldas¹⁷ on Al_2O_3 gels. It was found that the tendency to form monoliths is maximum at an acid/hydroxide ratio equal to 0.07. Interestingly, this ratio corresponds to the maximum in pore size and minimum in pore size variation.

Zarzycki²¹ compared three different drying procedures: slow drying, addition of surfactants during gelation, and hypercritical evacuation. The gels were prepared by hydrolysing tetramethylsilane in methanol with $\text{H}_2\text{O}/\text{TMS} = 4.65$. The most effective method for producing monolithic dried gels was found to be hypercritical drying. Such drying was effected by heating the gel with methanol in an autoclave to temperatures and pressures exceeding the critical point of methanol. In general, hypercritical drying produces dried gels with much larger pore volumes than that obtained by conventional evaporative drying. Because of the absence of liquid-vapour interfaces in case of hypercritical drying no capillary forces arise to cause network collapse and the net shrinkage during drying is very low.

Wang and Hench²² studied the principal mechanisms of sol-gel process which uses a drying control chemical additive (DCCA) in the sol to prevent fracture during drying. The system investigated was $20\text{Na}_2\text{O} \cdot 80\text{SiO}_2$ and the properties of gels made from this system with and without formamide as a DCCA were compared. A primary advantage of the DCCA in the gel is that the critical shrinkage rate is substantially higher. Consequently, the evaporation rate can be higher and drying times reduced several fold. The increase in critical shrinkage rate has been attributed to the formamide increasing the gel strength by amine group bonding of the gel particles.

In order to avoid crack during drying, double process of dispersion, drying and redispersion has been employed by Rabinovich *et al.*²³ for fumed silica (colloidal silica formed by flame decomposition of SiCl_4) sol-gel system. The material was dispersed using a blender in twice deionized water to form a sol. The pH of the sol was adjusted. Gelation was done by drying the sol at 150°C . The dried material crumbled and this material was redispersed to get a sol aging. After casting and gelation crackfree monolith was obtained. This effect of double process has been ascribed to the formation of an interconnected structure of pores in the $1\text{--}10\mu\text{m}$ size range allowing water evaporation without significant shrinkage.

Wall adhesion of the gel is another problem which needs thorough studies. Klein and Garvey²⁴ have proposed an idea of "floating" a gel on mercury in order to avoid stresses during shrinkage. Further research is needed in this area.

The drying behaviour of polymeric gels, such as those obtained by the acid catalysis of silicon alkoxide at low water contents can be considerably different with respect to those of colloidal gels. In these gels, the polymeric species are weakly crosslinked and as solvent is removed, they can deform readily and form a dense gel structure while the polymer itself shrinks and forms more crosslinks. The overall

result can be a dense dried gel with no large voids. Schaefer and Keefer²⁵ recently postulated that phase separation should be observed in such inorganic systems. However, the resulting phase separated structure may bear no relation to the structure of the gel originally formed in solution.

The pH of the initial solution has also an important role in the structure of dried polymeric gel. Fig 3 gives a schematic representation of gel desiccation²⁶ in acid and base conditions for polymeric gels, and the desiccation of colloidal gels under two particular conditions have also been shown.

Sintering

Depending upon the nature of the gel and the conditions of its formation, any of the following reactions may occur during firing: (i) decomposition of salts, (ii) carbonization or combustion of residual organic groups; (iii) desorption of absorbed solvent from the walls of micropores; (iv) dehydration (polymerization); (v) formation of micropores or even foams from gas generation; (vi) collapse of micropores; (vii) sintering and densification.

Yamane *et al.*²⁷ have recognized several temperature ranges of importance in the firing of silica gels prepared by alkoxide route. These are (a) 100–200 °C, desorption from the micropore walls of physically absorbed water, (b) 300–500 °C decomposition of organic compounds into CO₂; (c) 400–500 °C, collapse of small pores (d) 700–900 °C, collapse of larger pores. With non-optimized firing schedules, residual organic groups and H₂O can lead to blackening and fragmentation, as well as to the formation of bloated and foamed samples.

The densification of gel is a complex process²⁸. At least four mechanisms contribute to gel shrinkage: (a) capillary contraction; (b) condensation; (c) structural relaxation; and (d) viscous sintering. In case of borosilicate compositions, the above authors identified three temperature regions having different shrinkage rates. These are (i) 25–150 °C, weight loss with negligible shrinkage, (ii) 150–250 °C, shrinkage and weight loss, (c) 525–700 °C, dramatic shrinkage with little weight loss. Shrinkage in region (i) has been attributed to capillary contraction. Shrinkage in region (ii) is due to skeletal densification which occurs primarily by condensation reactions accompanying the loss of water and organic residue. According to these authors some amount of shrinkage in the temperature range 400–525 °C is due to structural relaxation. The rapid shrinkage in region (iii) is the result of viscous flow which permits the tiny pores in the gel to collapse. It should be noted that the processing variables during gelation may affect the shrinkage to some extent. Brinker and Scherer²⁹ found that gels prepared with low pH and low water of hydrolysis, which should be only modestly crosslinked, exhibit much greater densification at low temperatures than the more highly crosslinked gels prepared at high pH and high water of hydrolysis. Brinker and Scherrer²⁶ also observed that the amount of water and its distribution as well as heating rate are important to the kinetics of gel densification.

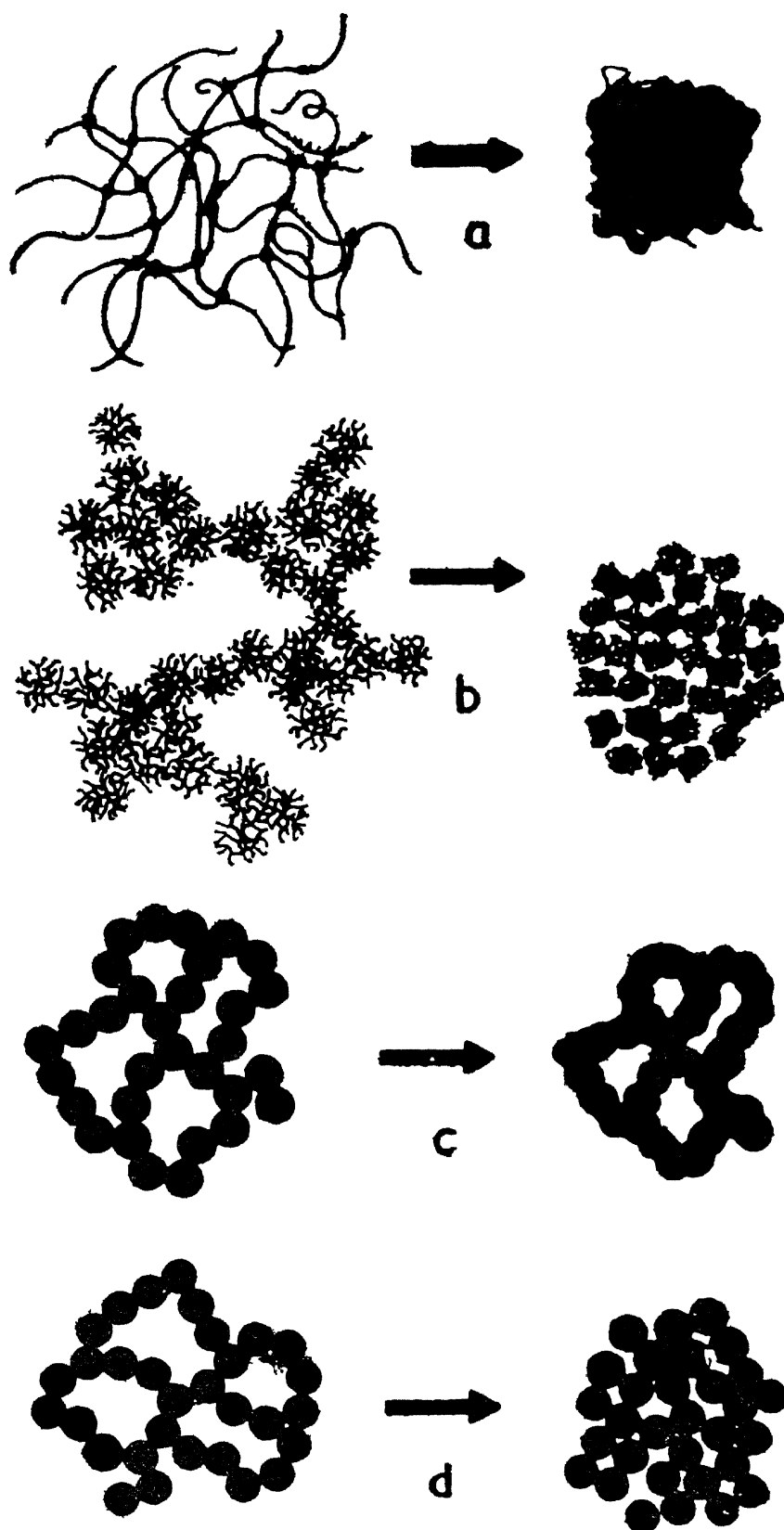


FIG 3 Schematic representation of gel desiccation for (a) acid-catalyzed gels, (b) base-catalyzed gels, (c) colloidal gel aged under conditions of high silica solubility, (d) colloidal gel composed of weakly bonded particles ²⁶

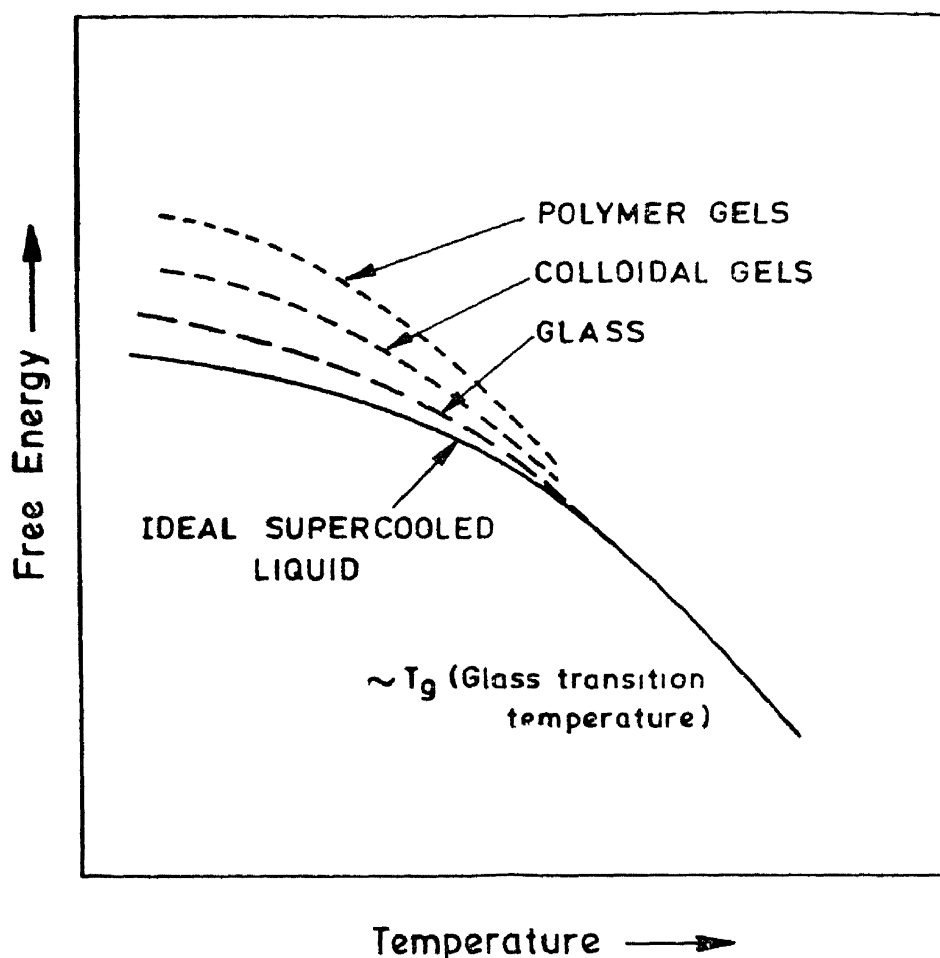


FIG 4 Schematic representation of free energy-temp relations between various desiccated gels, glass, and an ideal supercooled liquid of the same oxide composition ²⁶

Thermodynamically, xerogels (dried gels) may be considered high free energy materials compared to their dense oxide counterparts prepared by melting/sintering. The structural characteristics of the gel contribute to this high free energy. Surface area created by the formation of pores during desiccation makes the largest contribution toward this surface energy. Fig 4 gives a schematic representation of free energy vs temperature relations between various desiccated gels, glass, and an ideal supercooled liquid of the same composition.

SOL-GEL DERIVED MATERIALS

In the following sections, we discuss the preparation of different types of materials undertaken to date using the sol-gel technique.

Ceramics and Minerals

Since stoichiometry is controlled by the first step of the reaction between alkoxide partners the sol-gel technique is increasingly being applied to the synthesis of minerals and ceramics. The other favourable reason for this technique is the

possibility of low temperature densification of the solid due to the initial high surface energy of the gel particles

Using Al(OR)_3 and Ti(OR)_4 as raw materials, Duerksen *et al.*³⁰ prepared sintered titanate powder. This material is of interest to space and nuclear engineering due to its high temperature shock resistance and high negative temperature coefficient of electrical conductivity. Komarneni and Roy³¹ have reported a new sol-gel process for the preparation of TiO_2 gel spheres. The gel sphere preparation process involves the dispersal of the polymerized titanium ethoxide solution into a two phase liquid suspension in kerosene followed by heating in a microwave oven. The xerogel spheres obtained by this process were in the range of tens of micrometers in diameter. Spherical Na-Li aluminate particles have been successfully prepared³² by using sol-gel technique. ThO_2 and (U, Pu) O_2 microspheres have also been prepared by the sol-gel route.³³⁻³⁵ Suzuki *et al.*³⁶ synthesized mullite powder by calcination of the products of hydrothermal treatment of mixed alkoxide or mixed sol.

By co-precipitation of Al(OH)_3 and Mg(OH)_2 Bratton³⁷ was able to form MgAl_2O_4 (spinel). Dislich³⁸ prepared the same spinel *via* alkoxide route. Gels in the system Cr_2O_3 - Fe_2O_3 have been studied by Bhattacharya *et al.*³⁹ SiO_2 - Al_2O_3 catalyst has been prepared by Barrett *et al.*⁴⁰ by using sol-solution technique. Serpentine and related layer silicate minerals have been synthesized by Roy and Roy.⁴¹ Strictly stoichiometric mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) has been prepared by Mazdiyasnı and Brown⁴² through alkoxide route. Dense conductive β'' -alumina has been synthesized by Chen *et al.*⁴³ BaTiO_3 , KTaO_3 , KNbO_3 , K(Ta, Nb)O_3 , SrZrO_3 and PLZT, YIG ceramics have been prepared too.⁴⁴⁻⁴⁶ ZrO_2 - Y_2O_3 ceramics have been fabricated by Van De Graaf *et al.*⁸ by using metal alkoxide as precursors. Haaker and Ewing⁴⁷ have synthesized polycrystalline ZrSiO_4 , and are envisaging the synthesis of huttonite ThSiO_4 , Yttrialite $\text{Y}_2\text{Si}_2\text{O}_7$, Olivine Mg_2SiO_4 , and silicate oxyapatite $\text{CaLa}_4(\text{SiO}_4)_3\text{O}$. Pentlinghous used Si(OR)_4 (and other alkoxides)⁸² for the synthesis of NaBSi_3O_8 , which cannot be prepared in any other way since it melts incongruently. Likewise he prepared Mg_2GeO_4 , CsAlSiO_4 , $\text{CsAlSi}_2\text{O}_6$, $\text{CsAlSi}_5\text{O}_{12}$. SiO_2 - Fe_2O_3 system has been studied by Guglielmi and Principi⁴⁸. Sol-gel method has also been employed to fabricate high-field ZnO varistors⁴⁹ and improved ferrite memory-cores.⁵⁰

For materials whose alkoxides are either difficult to make or use, or are too expensive, the method of McCarthy and Roy⁵¹ may be employed to incorporate them into a gel. These workers added the materials to a solution of alkoxides in the form of chlorides, nitrates, sulphates or acetates. This approach was adopted by Hayashi and Saito⁵² who produced gels in the CaO-SiO_2 system by mixing TEOS (tetraethyl-orthosilicate) and $\text{Ca(NO}_3)_2$ in ethanol.

Glasses

Gel-derived powders are used as batch ingredients for glass melting primarily because of the high degree of chemical homogeneity which they offer. This leads to shorter melting times and lower melting temperatures as well as compositional

uniformity In sintering or hot pressing amorphous gel derived powders, the key to glass formation is the development of an appropriate heat treatment schedule to remove the residual organic groups and achieve pore collapse without inducing crystallization These often indicate an upper limit to temperature for processing, above which crystallization precludes the achievement of complete densification as a glass.^{53,54}

The physical properties of gel derived glasses are very similar to those of glasses obtained from a melt²⁷ But there are notable differences in kinetic behaviour between gel-glasses and melted glasses Mukherjee *et al*⁵ found that gel derived glasses exhibit a much more uniform microstructure and finer scale of phase separation than corresponding melted glasses In addition, the rates of crystallization of the gel-derived glasses were much higher than those of melted glasses The differences in kinetic behaviour were associated with higher OH content of the gel-derived glasses⁵ Weinberg and Nelson⁵⁵ reported a marked difference in liquidus temperature between gel-derived and melted glasses Hench *et al*.^{53,54} noted that the aqueous corrosion resistance of gel-derived glasses was considerably less than that of melted glass Gottardi *et al*.⁵⁶ found a sharper glass transition in gel-derived glasses, reflecting a narrower distribution of relaxation times, compared with melted glasses

Apart from the conventional glasses like SiO_2 , $\text{SiO}_2\text{-Al}_2\text{O}_3$, $\text{SiO}_2\text{-P}_2\text{O}_5$, $\text{SiO}_2\text{-P}_2\text{O}_5$, $\text{B}_2\text{O}_3\text{-P}_2\text{O}_5\text{-Na}_2\text{O}$, $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-K}_2\text{O-Na}_2\text{O}$ etc.,¹⁰ many novel glasses have been developed by the sol-gel technique. Glasses in the system $\text{BeO-CeO}_2\text{-ZrO}_2$ have been reported⁵⁷ Hayashi and Saito⁵² have prepared glasses in the system CaO-SiO_2 In this case, transparent glasses were obtained of compositions in the field of the liquid-liquid immiscibility gap, which require very high melting temperatures (2000 °C) and even then are obtainable only as a grossly two-phase or partly crystallized glasses. Glasses in the system $\text{Na}_2\text{O-ZrO}_2\text{-SiO}_2$ containing high ZrO_2 (upto 33 wt per cent) have been fabricated by Kamiya *et al*^{58,59} Makashima *et al*⁶⁰ studied glasses in the system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-ZrO}_2$

Superionic glasses have been prepared by Boilot *et al*⁵⁹ via sol-gel process using alkoxides as raw materials. The systems studied were $M_2\text{O-M}^1\text{O}_2\text{-SiO}_2\text{-P}_2\text{O}_5$ ($M = \text{Li, Na, K, } M_1 = \text{Zr, Ti}$) and $\text{Li}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{-P}_2\text{O}_5$. These glasses were made by heating gels above 400 °C and they generally remain stable upto 700 °C

Chi⁶¹ was able to synthesize carbon containing glasses by inert atmospheric pyrolysis of glass precursors (dry gels) made from methyltrimethoxysilane and colloidal silica Brinker *et al*^{62,62a} obtained oxynitride glass when porous, multicomponent silicate gels were heated in flowing and pressurized NH_3 These treatments resulted in dense, homogeneous oxynitride glasses which were synthesized at low temperature (≤ 1000 °C) without melting

Transparent microporous silica has been fabricated by Klein *et al*⁶³ These porous glasses can be used as supports for catalysts. The sol-gel procedure also offers the possibility to encase radioactive waste material in glass⁶⁴

Ohno *et al.*⁶⁵ fabricated micron order relief patterned SiO_2 glass using a sol-gel process. The relief pattern was clearly replicated from a master pattern onto the SiO_2 glass surface.

Another kind of sol-gel technique is the fabrication of thin-walled glass hollow spheres. Such spheres (diameter 80–100 μm , wall thickness 1 μm) are inflated and formed by gases originating from the gel.⁷ Deuterium-tritium fuels can be stored within such hollow spheres for thermonuclear fusion.⁶⁶ Also hollow glass supports for growing cell cultures have been made by using sol-gel technology.⁶⁷

Glass-Ceramics

In 1971, the first glass-ceramic synthesis by sol-gel route was reported by Dislich,⁷ meanwhile numerous syntheses have been reported. For example, partially ceramized glasses were described by Gottardi *et al.*⁶⁸ in the system $\text{Na}_2\text{O}-\text{Cr}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{ZrO}_2$. In addition to glass phase, tetragonal and monoclinic ZrO_2 , ZrSiO_4 , $\text{Al}_2\text{O}_3/\text{Cr}_2\text{O}_3$ are obtained as crystalline phase, depending on the composition and heat treatment temperature. As a result of the higher homogeneity and reactivity possible in the sol-gel procedure, these phases are formed at relatively lower temperature.

Glass-ceramics in the system $\text{SiO}_2-\text{Al}_2\text{O}_3-\text{MgO}$, containing high quartz, low quartz and spinels as crystalline phases (small amount of TiO_2 and Li_2O were added to the glass compositions) have been studied by Holand *et al.*⁶⁹

Coatings and Thin Films

Since drying stresses can readily be accommodated for thin gel layers, the use of gel techniques to produce coatings has acquired much importance. Using gel techniques, antireflection films with attractive properties have been prepared by a number of workers. These include single layer $\text{TiO}_2-\text{SiO}_2$ films,⁷⁰ $\text{SiO}_2-\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ films.⁷¹ Multilayer $\text{TiO}_2-\text{SiO}_2$ films^{72,73} and $\text{BaO}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2$ films of Brinker *et al.*^{73,74}

Gel technology has also been exploited to make protective coatings. Interesting examples are $\beta\text{-Al}_2\text{O}_3$ coating^{71a} on substrates to enhance mechanical and chemical properties, CeO_2 coating to gas cooled reactor materials for environmental protection,¹⁰ coatings of Al_2O_3 on silicon carbide and silicate glass fibres,^{75–77} Si_3N_4 coatings on quartz and sapphire,⁷⁸ expansion adjusted $\text{SiO}_2-\text{GeO}_2$ coatings (for protecting nonoxide ceramics against oxidation at high temperature)⁷⁹

Sol-gel process has been employed to form siliceous membranes at the surface of filter media to improve their filtration properties.⁸⁰ Similar technique has been used by Carturan *et al.*⁸¹ to coat glass microspheres with thin layers of porous oxide, and such materials can be used as supports for catalysis.

Gel derived coatings have also been studied to modify the optical and electrical properties of materials. Some interesting examples are colloidal palladium embedded TiO_2 coatings on float glass (to have desired absorbance of visible light), IR reflecting ITO (Indium Tin Oxide) coatings,^{81,82} Optoelectronic PLZT films,⁸³ transparent, electrically conductive cadmium stannate,⁸⁴ tin dioxide⁸⁵ coatings.

Sol-gel method can also be employed for coating glass fibres. Guglielmi and Maddalena exploited the sol-gel technology to coat E-glass fibres with a $\text{SiO}_2\text{-ZrO}_2$ film. These fibres can be used for cement composites.

The use of sol-gel techniques on the production of free standing films has been surveyed by Sakka.⁸⁷ Several techniques for making such films have been developed, including (a) pouring alkoxide solutions onto liquids which do not mix with the solution and allowing the film to hydrolyze, (b) pouring the solution onto non-wetting surfaces such as Teflon, and (c) forming films using wire rings with solutions of appropriate viscosity.

Fibres

Both polycrystalline as well as glass fibres have been prepared by sol-gel method. Using appropriate conditions, continuous fibres may be drawn from solutions of metal alkoxides. Fibrous gels are converted to glass fibres by heating. In many cases, heating of the gels produces a blackening of the fibres, very likely associated with fine carbon particles. Their formation can, however, be suppressed by heating the gels immediately after fibre drawing before further polymerization can occur.^{58,58a}

Glass fibres have been fabricated in the systems SiO_2 ,^{88,89} $\text{SiO}_2\text{-Al}_2\text{O}_3$, $\text{SiO}_2\text{-TiO}_2$,^{89,89a} $\text{SiO}_2\text{-ZrO}_2$, $\text{SiO}_2\text{-ZrO}_2\text{-Na}_2\text{O}$ ^{58,58a}

Kokubo *et al.*⁹⁰ have developed a method for preparation of amorphous ZrO_2 . Zirconia hydrogel was made from ZrOCl_2 solution. The gel was placed in a plastic cylinder and unidirectionally frozen by lowering the cylinder into a -78°C cold bath at 4–6 cm/hr. A bundle of parallel fibres longer than 8 cm and 10–60 μm in diameter was obtained after thawing. The fibres were amorphous and porous as dried at 25°C . Their pores were greatly eliminated by heat treatment in vacuum at 290°C for 2 days. The chemical composition of the heat treated fibres was approximately $\text{ZrO}_2 \cdot \text{H}_2\text{O}$.

As extreme purity is needed for telecommunication glass fibres, there is a strong tendency to produce performs by the sol-gel process, from which the fibre is drawn subsequently by melting.^{7,91}

Polycrystalline $\alpha\text{-Al}_2\text{O}_3$ fibres have been prepared by Blakelock *et al.*⁹² by extruding gelled solutions through dies of appropriate diameter and sintering the resulting fibres at 1750°C . Polycrystalline fibres in the systems $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-SiO}_2$ ⁹³ as well as mullite $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, and aluminoborosilicate $3\text{Al}_2\text{O}_3 \cdot \text{B}_2\text{O}_3 \cdot 3\text{SiO}_2$ have been reported. Fibres in the systems $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-ZrO}_2$, $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-TiO}_2$ and $\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3\text{-SnO}$ have also been investigated by Sowman.⁹⁴

Fine grained metastable tetragonal ZrO_2 fibres have been drawn by Leroy *et al.*⁹⁵ Such fibres were obtained by extrusion and air-jet drawing of an aged (polymerized) concentrated solution of zirconium acetate.

Mahler and Bechtold⁹⁶ obtained silica fibres by directional crystallization of silicic acid solutions. The polysilicic acid-rich material is rejected at the ice-water

interface, and undergoes accelerated concentration-dependent polymerization. As a result, it becomes insoluble, and after thawing, it retains the structural forms developed during crystallisation.

Composites

Fibre-reinforced sol-gel derived aluminium oxide composites have been fabricated by Lannutti *et al*⁷⁵⁻⁷⁷. In case of short ceramic fibres and whiskers (ZrO_2 , SiC, graphite), they were uniformly dispersed in a low viscosity sol and then frozen into the matrix via geleation. For long fibres, preforms were placed in trays and subsequently liquid alumina sol was added and gelled.

Roy and Roy⁹⁷ prepared ceramic-metal composites from diphasic xerogels. The final microstructure consisted of noncrystalline (in a few cases, microcrystalline) ceramic matrix with small metallic islands (5–50nm) and micro (and macro) pores. Such “nanocomposites” have been obtained in SiO_2 , Al_2O_3 , ZrO_2 systems containing metallic Cu, Pt, Sn and Ni.

Datta *et al*⁹⁸ have prepared glass-metal microcomposites containing nickel islands (5–30nm) dispersed in a silica matrix.

Abrasives

Leitheiser and Sowman^{97a} employed sol-gel techniques to produce non-fused alumina based abrasives with a microcrystalline structure of randomly oriented crystallites. After gelation and drying, the material was crushed and sized. The sized powders were then fired, typically in the range of 1250–1300 °C. In this way, Al_2O_3 abrasive particles with uniformly dispersed ZrO_2 particles were obtained. Such abrasive particles showed superior grinding performance compared with fused or sintered Al_2O_3 -based abrasives.

Breval *et al*⁹⁹ prepared single phase Al_2O_3 and 2-phase Ni—, NiO—, and $\text{NiAl}_2\text{O}_4\text{Al}_2\text{O}_3$, and AgCl— SiO_2 abrasive grains through sol-gel process.

NEWER APPLICATIONS

In the field of refractories, sol-gel process may be employed to get better results. One such attempt was made by Selyanko *et al*.¹⁰⁰ They used sol-gel process for the manufacture of binders from AlCl_3 solutions by hydrolysis with MgO or NH_4OH in high Al_2O_3 grog.

In order to get ultrapure homogeneous glasses, the recent trend is to exploit containerless melting in space. Because of the absence of gravity induced convection currents, the homogenization of glass using conventional raw materials is difficult in the space environment. Multicomponent, homogeneous, noncrystalline oxide gels can be prepared by the sol-gel process and these gels are promising starting materials for melting glasses in space environments (Batt. Col. Lab.)¹⁰¹

Sol-gel method seems to open a new way in the field of biomaterials technology. The lower temperature range of gel glass synthesis makes it possible to get inorganic-

organic glasses Recently, Philipp *et al*¹⁰² fabricated such glasses (e.g., epoxysilane-titanium orthoester) for hard contact lenses

Other prospective products¹⁰³ are nonoxide communication fibres, controlled release medications, photo and electrochromics, electrical and magnetic devices from transition element gels etc

CONCLUDING REMARKS

Though sol-gel process has made an impact on materials technology as well as on novel materials exploration the high cost of alkoxides seems to be an hindrance for its large scale use in preparing conventional materials It will be worthwhile to find out whether alkoxide route can be substituted by a more economic one.

The sol-gel process should also be tried in nonaqueous media to explore the possibilities of preparing novel materials Such experiments have been tried in a few cases. Bonner *et al.*¹⁰⁴ prepared fumed silica gels with a wide variety of nonaqueous liquids like methanol, ethanol, propanol, ethyl glycol etc. Brinker¹³ replaced water by ammonia (hence ammonolysis in place of hydrolysis of sol-gel process) and in the process got nitrides and oxynitrides This area should be explored in a systematic way

Since many of the interesting ceramic materials which can be obtained from gels consist of several chemical components, it is imperative that advantage be taken of complex precursor formation Hence, detailed studies should be done on formation of complexes and characterization of reaction products in multi-component systems

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CHEMICAL BOND AND THE NATURE OF INORGANIC GLASSES*

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Bonding in inorganic glasses is generally a mixed ionic-covalent type. In highly ionic glasses intermediate range order develops with the formation of clusters. In covalently bonded glasses, formation of charged defects plays a significant role in many glass properties. Covalency itself appears to increase in the glassy state. In this article, examples of the consequences of the type bonding on the structure and stability of glasses have been presented. Inherent glass-forming tendency in several inorganic compounds is also discussed in the light of a chemical model.

Key Words : Chemical Bond; Inorganic Glasses; Intermediate Range Order, Covalency; Octahedral Motifs

INTRODUCTION

A number of inorganic systems are known to form glasses¹⁻³. They are generally characterized by overwhelming chemical and structural complexity and elucidation of general principles governing the glassy state is not easy. There are, however, several chemically simple materials also which easily vitrify, for example, simple elements like S and Se, oxides like B₂O₃, SiO₂ and P₂O₅, chalcogenides like As₂S₃ and As₂Se₃ and halides like BeF₂ and ZnCl₂. They are mostly covalently bonded and considered to possess good glass-forming tendency. A similar tendency to vitrify is not prevalent among simple ionic materials. Even the simplest ionic glasses are typified by those formed in binary nitrates, KNO₃-Ca(NO₃)₂ and sulphates K₂SO₄-ZnSO₄ and are fairly complex⁴⁻⁶. Further, glasses are formed only in certain restricted composition regimes with relative ease. It is common practice in glass literature to use descriptions like glass formers, glass-forming tendency etc. Such terms, although quite generally understood, are rather non-quantitative in the real sense. We have assumed for the present purpose that melts which vitrify with cooling rates not greater than 1000deg/sec are good glass formers.

There is thus an apparently strong influence of the nature of bonding on the vitrification of the materials. In our investigations of a number of inorganic glass systems, a few important features revealing the relation of bonding to the structure

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and properties of glasses have been noted. These features have been discussed particularly in the context of some of the problems of the glassy state such as inherent glass-forming tendency in some materials.

INORGANIC GLASSES AND CLUSTER FORMATION

Typical ionic glasses are formed in mixed sulphates K_2SO_4 - Na_2SO_4 - $ZnSO_4$ and in AgI - Ag_2MoO_4 ; the latter is an example of a fast ion conducting glass.^{7,7a} They all contain discrete anions like SO_4^{2-} and MoO_4^{2-} . An important feature of ionic glasses is that the interaction is through non-directional and long-range coulombic forces. The long-range nature of the interactions in some way appears to induce nucleation of ordered crystalline regions. It, therefore, makes it almost impossible to quench simple ionic melts like $NaCl$ into glasses. In quenching binary or ternary melts advantage is taken of the fact that long-range diffusion required for growth of large crystallites of stable crystalline phases does not occur in the time-scale of cooling kinetics. Ionic glasses so obtained can be modelled using cluster model in which a glass is assumed to possess a cluster-tissue texture. Clusters would correspond to highly ordered, essentially crystalline regions whose spatial extension of 10-100 Å. Material present in the inter-cluster region is assumed to be truly amorphous and described as connective 'tissue' which possesses somewhat lower density. Normally the tissue is either enriched or impoverished compositionally though to a small degree with respect to atleast one mobile ionic species.⁸⁻¹⁰

Presence of fine clusters with crystalline order has been indirectly evidenced in AgI - Ag_2MoO_4 glasses^{11,12}. But it is not essential that clusters should possess only a crystalline order. High degree of positional correlation of the ions is sufficient to describe it as a cluster. Such clusters called 'amorphons' could result from restrictions of ionic packing also. In sulphate glasses where a modified random packing model was found to serve as an adequate structural model, Zn^{2+} ions are coordinated always to six oxygen ions from six SO_4^{2-} ions in an octahedral geometry while K^+ and Na^+ ions are coordinated to 12 and 8 oxygens respectively from 4 surrounding SO_4^{2-} ions.⁴⁻⁶ Structures built with such features are unlikely to develop crystalline clusters with uniform composition. It may result in the formation of amorphons. Within the amorphon positional correlation of ions is very high. Amorphon clusters would be held together by disordered tissue-region of slightly lower density and again a cluster-tissue texture would ensue.

The presence of discrete anions and cations interacting coulombically would therefore give rise to a cluster-tissue texturing on an extremely fine scale. Formation of clusters in a variety of glasses (including ionic glasses) has been evidenced in many experiments. For example, in highly modified silicate glasses¹³ and metallic glasses¹⁴ fringe patterns have been observed in high resolution electron microscopy suggesting presence of highly ordered regions. Freezing of the spin-spin correlation times prior to thermal glass transition upon cooling of glass-forming

melts doped with tempone has been noted in ESR experiments in organic glasses,¹⁵ suggesting formation of clusters in supercooled liquids prior to the incidence of glass transition. Evolution of roto-diffusive motions of sulphate ions in the tissue and on the cluster surfaces at a temperature below the thermal glass-transition while heating the samples has been noted in IR spectroscopy.¹⁶ The pressure has been found to transform the tissue into clusters leading to total crystallization resulting in the expected conductivity changes in AgI-Ag₂O-MoO₃ glasses.^{11,12} The high pressure studies have provided a remarkably unique evidence for the presence of clusters. A large number of direct and indirect evidences with regard to clustering in a variety of glass systems have been discussed by Phillips.¹⁷

The cluster tissue texture may thus be assumed to be a common feature of all ionic glasses. The cluster-tissue texture may inherit both density and compositional differences between the two regions. Cluster model has been treated quantitatively in order to investigate glass-transition phenomenon.^{8,10}

Glass-transition itself is a characteristic thermal event occurring in glasses at a temperature which is roughly about 2/3 of the liquidus (or melting) temperature of the corresponding crystalline phase.^{18,19} The transition in most real glasses is diffuse in comparison to solid-solid phase transitions in crystalline materials. However, step like changes occur in heat capacities and thermal expansivities which often give the impression that the underlying phenomenon shares features of a second order transformation.²⁰ The problem of glass-transition in the cluster model is addressed via its vibrational properties.¹⁰ The less dense, disordered, tissue region is assumed to be characterized by highly anharmonic potential wells. As a result, potential energy wells coalesce at higher vibrational levels. Correspondingly, systematic increases occur in amplitudes along with decreased energy separations. At sufficiently high potential energy levels, the amplitudes and times of oscillations become very large and any uncorrelated random displacement in the neighbourhood can wipe out the memory of the vibrating species. Hence, a vibrational mode is converted into a translational mode. The occupancy of vibrational levels is a function of temperature. With increasing temperature, particles in ground vibrational state are excited to higher levels and the loss of particles from the ground vibrational state is replenished from the surfaces of the clusters which share features of anharmonicity on the side of the tissue. In other words, as the temperature is increased, particles in the tissue regions are excited to large amplitude states in coalesced potential wells providing for smooth evolution of translational modes from vibrational modes. This is followed by a continuous 'turning in' of particles from the cluster surfaces into the cauldron of the tissue, whose volume increases at the expense of the shrinking clusters. The rate of shrinking and thus the rate of the whole process increases rapidly towards the end when the clusters disappear, terminating in the glass transition.

With very few and plausible assumptions, this model has been used to show that

$$\xi = a^{1/3} \left[1 - \frac{(a-1)Z}{a} \right]^{1/3},$$

where $\xi = (\bar{r}_e^T / \bar{r}_e^0 = [\langle V_e^T \rangle / \langle V_e^0 \rangle]^{1/3}$

represent the ratio of the average radius of the cluster at temperature T to its average radius at $0K$, a is equal to the ratio of the total volume of glass to the total volume of the cluster at $0K$ and Z is the relevant partition function for the tissue region. ξ has been found to behave like an order parameter decreasing rapidly towards the glass-transition temperature, T_g . Hence, it would be profitable to associate ξ with the notion of a coherence length of a phonon mode so that in the reverse direction (while cooling) the glass transition exhibits a divergence in ξ producing the likeness of a mean field governed transition (Fig. 1).

Employing heuristic but plausible energy manifold for the partition function, heat capacity variations for a cluster tissue glass have been evaluated which seems to simulate reasonably well the behaviour of real glasses. The glass transition in the model is controlled by the ground state vibrational frequency of the most mobile ion in the glass, for example, alkali ions in most alkali containing glasses. It could also be an anion such as halogens in lead oxyhalide glasses. If ΔE is the ground state vibrational energy of the mobile ion then,

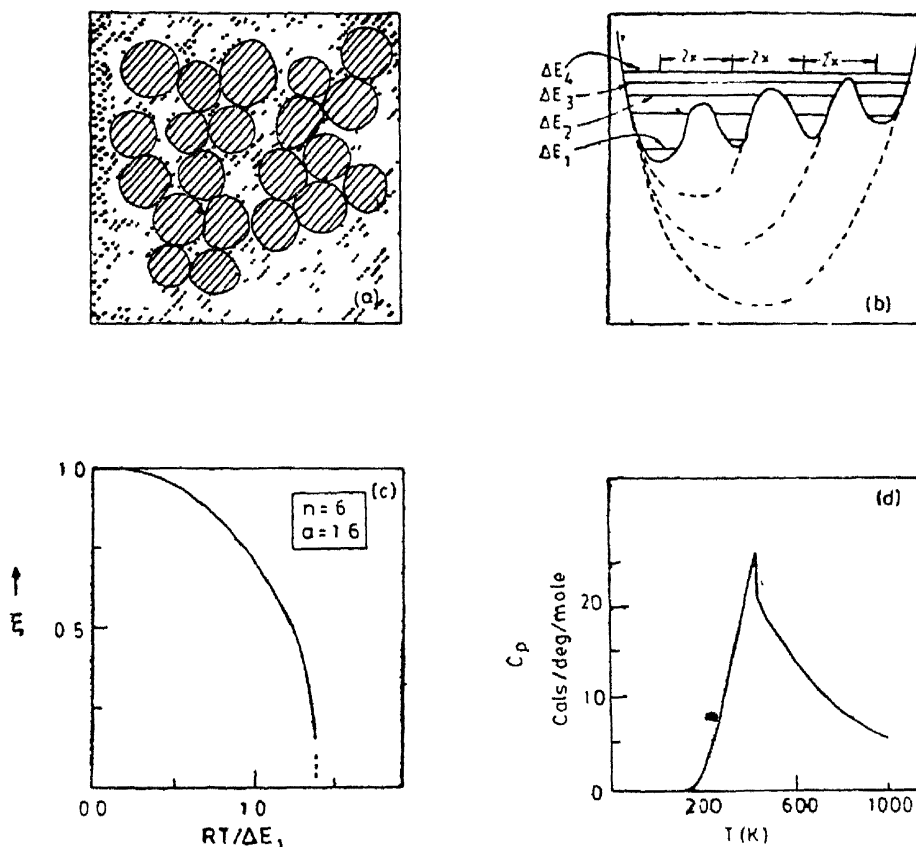


FIG 1 Cluster model of glasses¹⁰ (a) a schematic illustration of cluster-tissue texture, (b) a schematic of anharmonic potential wells which coalesce at higher energy levels. Energy differences ΔE_1 , ΔE_2 etc decrease and amplitudes (number of times $2x$) increase in higher vibrational levels, (c) variation of ξ with reduced temperature $RT/\Delta E$ (a is taken as 1.6 and number of vibrational states 6), (d) typical variation of configurational heat capacity in the model

$$T_g = \frac{CR}{\Delta E},$$

where R is gas constant and C is a constant of the model whose value is between 1.2 and 1.6. It is interesting to note that T_g cannot exceed about 1110 K in view of the highest known cage vibrational frequencies. Ionic glasses have frozen entropies whose magnitudes are considerably low²¹. This is consistent with the cluster model. Since the clusters are highly ordered or microcrystalline, the glass can sustain only small magnitudes of configurational entropy in its tissue region which forms a minor component particularly in well-annealed glasses.

A further advantage of such a model is that the notion of soft mode²² can be introduced in a natural manner to discuss the behaviour of glasses. As noted earlier, ions which populate systematically coalesced potential energy states with systematically increasing degree of coalescence possess systematically lower vibrational frequencies and their values ultimately approach zero towards T_g . Such are the soft modes germane to glass and their character is different from that of soft modes in crystals. Temperature behaviour of Lamb Mossbauer factors in glasses²³ can be understood on the basis of such soft modes.

CHARGED DEFECTS AND COVALENT GLASSES

Arsenic chalcogenides form typically covalently-bonded glasses. Particularly interesting are the series of glasses formed in As-Se system, all the way from Se to significantly As-rich ($\text{As}_{80}\text{Se}_{20}$) compositions. The structure of these glasses correspond to As-Se networks in which As is 3-coordinated and Se is 2-coordinated. A feature of structural interest in these glasses is that in compositions away from stoichiometric As_2Se_3 , homoatomic bonding is to be expected as indeed the case. Since the energy of the heteroatom bond, As-Se, is significantly different and greater than energy of either of the homoatomic (As-As and Se-Se) bonds, maximum heteroatom bonds are first formed in the melt so that homoatomic As-As bonds are absent in Se-rich glasses and vice versa (Fig 2)²⁴ a situation described as 'chemical ordering'²⁵ and is present in most chalcogenide glasses since heteroatom bond energies are higher than the pertinent homoatomic bond energies (by several times kT_m). Increase in electronegativity differences between the elements in glasses gives rise to increase in the ionic character of the bonds and hence, the heteroatomic bonding dominates. In fact, the ionic energy component due to heteroatom linkages can be so high that in oxide glasses, neither peroxy linkages nor the corresponding homoatomic counterpart (such as Si-Si, B-B etc linkages) coexist in the glasses formed from the high temperature melts due to their relative instability. Another feature of significance in covalent glasses is the constancy of local coordinations in their structures. By and large they remain fixed as for example $[\text{SiO}_4]^{2-}$ tetrahedra, $[\text{AsSe}_3]^{2-}$ pyramids, etc. The covalent network can be 1 or 2 or 3 dimensional as typified by S, As_2Se_3 and SiO_2 . Glass properties, however, are isotropic due to the randomness in packing which eliminates the directionalities.

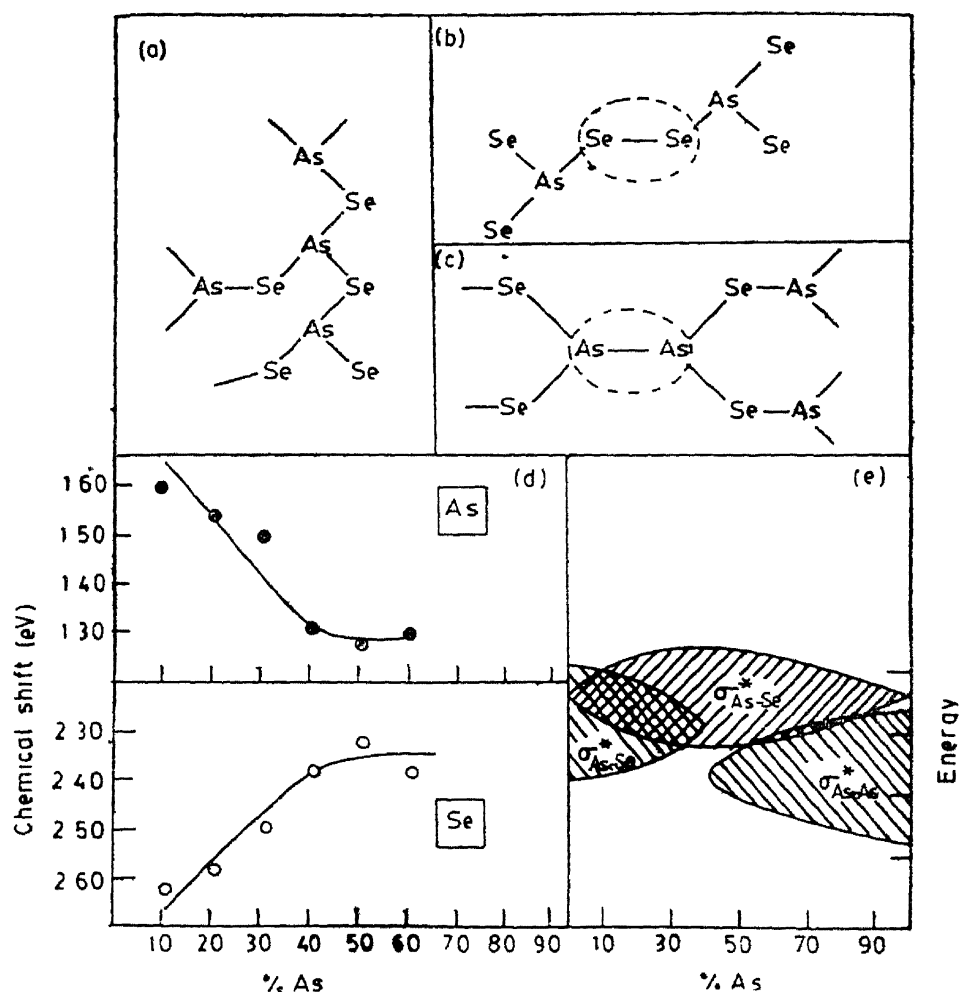
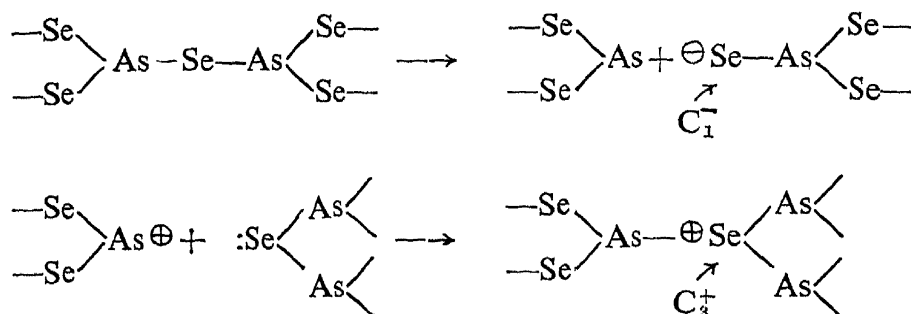


FIG 2 Chemical ordering in As-Se glasses (a) structure of stoichiometric As_2Se_3 glass (b) structure Se-excess glass (c) structure of As-excess glass (d) variation of chemical shifts of As and Se in As-Se glasses as a function of composition, (e) a schematic of band energy diagram which is used to explain behaviour of chemical shifts²¹

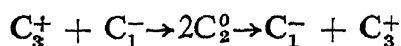
From a topological point of view, crystallinity of the covalent networks can in general be eliminated through introduction of either bond angle or bond length distributions. Comparison with model structures at least in fused quartz strongly support a spread in Si-O-Si bond angles.^{26,27} In glasses of lower network dimensionality such as Se and As_2Se_3 inter network bonding is also significant. Indeed in As_2Se_3 the behaviour of glass-transition could be explained reasonably quantitatively by the excitation of inter layer secondary bonding²⁸

It is now known that all covalently bonded glasses are characterized by defects. The investigation of electron-transport in semiconducting chalcogenide glasses led to a more detailed formulation of these defects. Electron transport in chalcogenides was once thought to involve electrons present in 'dangling bonds' created by the homolytic scission of bonds. These localised electrons were supposed to populate levels in the gap^{29,30}. Since electron spin resonance studies do not support the presence of unpaired spins consistent with the magnitude of conductivity, it was

postulated that dangling bonds redistribute electrons creating charged defects^{31,32}. This in chemist's language is the heterolytic bond breaking.¹ Chalcogenides carrying lone pairs of electrons readily coordinate to the positive species created in bond breaking thereby restoring the loss of covalent bond as shown below :



The net effect is the creation of a defect pair, C_3^+ and C_1^- (where C is the chalcogenide), the over- and under-coordinated chalcogenides respectively at a net expense of energy required for pairing electrons in the valence orbital of the chalcogen. Such pairs of defects as known as conjugate pairs of defects^{33,34} which we believe play a dominant role in covalent chalcogenides glasses. Consider, for example transport could occur through the reverse process in which defects are annihilated and recreated by the reaction

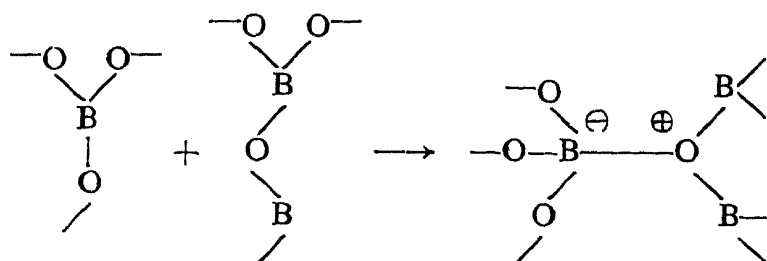


The reaction occurs with neutral state as activation stage, the recreated pairs could be present at a point further down in the direction of the field and the process amounts to transfer of a charged centre or two electrons (or equivalently two holes). The activation barrier would, therefore, correspond to the energy required for the creation of defect pairs. Indeed, the experimental d.c. conductivity activation energies have been shown to be equal to the energy required for creation of conjugate pairs of defects in a large number of amorphous chalcogenides³³. The conductivity is due to thermally assisted hopping of charged defects which are bipolarons. This aspect has been confirmed through linearity of $\log \sigma T^{-2/5}$ plots³⁵.

The primary feature of charged defect model is that it conserves the total number of covalent bonds at the expense of a relatively lower energy required for electron pairing. What is not usually as well appreciated is that charged pair creation brings two more bonus advantages for the glassy state. Firstly, it allows for snapping of a covalent bond where an inconvenient degree of bonding strain develops during the growth of amorphous structure. This is crucial in ridding ordered arrangement of atoms. Secondly and more importantly, it introduces charged centres which provide for additional ionic interactions while conserving the total number of covalent linkages. This stabilises energetically the glass network. Such defects, therefore, may be a common feature of all glasses which contain lone pair bearing elements like oxygen and chalcogens. In silica glass, for example, formation of conjugate pairs charged defects like $[\text{O-Si}_{3/4}]^+$ and $[\text{O-Si}_{1/4}]^-$ centres

may help terminate the strains created by cumulative distortion effects upon basic quartz structure. A model of SiO_2 glass would, therefore, suggest presence of clusters of essentially quartz-like structure mediated by thin walls of tissue consisting of a large density of conjugate defect pairs of over- and under-coordinated oxygen. It is worth examining whether such defect pairs are responsible for some of the anomalous properties of fused quartz.³⁶

It is well known that B_2O_3 can be crystallized only with difficulty³⁷ and melts of B_2O_3 exhibit properties consistent with fluids with three-dimensional networks³⁸ rather than with two-dimensional networks. It would be tempting to attribute these features to the additional bonding made possible through charge defects of the following type —



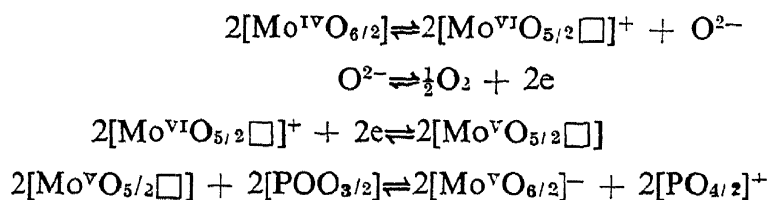
Formation of tetrahedral boron through participation of the lone pair on oxygen should be exothermic combining both covalent and coulombic interactions. Presence of such stable defects therefore may generate a structural resistance to nucleation of the crystalline B_2O_3 melts. It would also account for the three-dimensional network character of B_2O_3 melts. We shall see a little later that charged defect pairs which interact through coulombic forces play a significant role in molybdophosphate glasses also.

GLASSES WITH OCTAHEDRAL MOTIFS

It has been the general belief that in glasses coordination numbers are low (2 to 4) in conformity with Zacharisen's model. We have already noted that in ionic glasses which are dominated by non-directional bonding, the participating ions tend to acquire maximum coordination subject only to geometrical constraints. Therefore, an ionic glass, constitutes an antithesis of Zacharisen's glasses. Even in cases where covalency of bonding dominates, as in the novel glass systems like molybdophosphate and lead oxyhalides octahedrally coordinated structural units form the primary motifs. In fast-ion conducting $\text{AgI-Ag}_2\text{O-MoO}_3$ glasses molybdenum is present in discrete MoO_4^{2-} tetrahedral ions. But in this glass system, the oxygen ion activity is high and stabilizes the tetrahedral MoO_4^{2-} .^{7,39} In molybdophosphates, however, due to high formal valence states of phosphorous and molybdenum, metal-oxygen linkages are largely covalent. In the absence of oxygen ion activity Mo is present in formally neutral $[\text{MoO}_6/2]$ units in which hybridized d^2sp^3 -orbitals of Mo are used for bonding with oxygen. Equimolar $\text{MoO}_3\text{-P}_2\text{O}_5$ glass corresponds to chemically ordered network of $[\text{MoO}_6/2]$ and $[\text{POO}_3/2]$ units with all but two

corner shared oxygen.⁴⁰ One of the oxygens in $[\text{POO}_{3/2}]$ units are attached to the phosphorus atom through a double bond. Mo-O bond is as covalent as Si-O bond and the structure is therefore adequately described as a three-dimensional covalent network. The effect of modifiers may be discussed in the same manner as in silicate glasses. Modification with alkali oxides which release O^{2-} ions for bond-breaking increases the oxygen ion activity and when more than two -Mo-O-Mo- or -Mo-O-P- linkages are broken, resulting $[\text{MoC}_{4/2}\text{O}_2]^{2-}$ units convert themselves into $[\text{MoO}_4]^{2-}$ units. Conversion is easy because $[\text{MoO}_4]^{2-}$ units have roughly the same rotational volume as occupied by $[\text{MoO}_{6/2}]$ units. Conversion of $[\text{MoO}_{4/2}\text{O}_2]^{2-}$ units are both evidenced in IR spectra and inferred in several properties of glasses.⁴⁰

Mo^{6+} is often reduced with facility to Mo^{5+} at the higher temperature employed for the glass preparation. This reduction leads to loss of oxygen. The glasses formed are quite stable, coloured and give rise to characteristic ESR spectra. Here also charged defect pairs, but of a slightly different nature appear to play an important role.⁴⁰ While the octahedron around Mo^{5+} is negatively charged, the structure of octahedron is retained without the loss of a corner by the ready participation of an otherwise unshared oxygen attached to phosphorus through a double bond. The process may be represented as follows —



In the process, $[\text{POO}_{3/2}]$ unit is converted into $[\text{PO}_{4/2}]^+$ unit and is paired to $[\text{MoO}_{6/2}]^-$ unit. By the creation of such paired defects, structural features are retained, coulombing energy term is added and further cross-linking is achieved through 4-connected phosphate units.

The apparently facile nature of the conversion of $[\text{POO}_{3/2}]$ unit into a charge bearing $[\text{PO}_{4/2}]^+$ is exploited by additives like PbO which possess a tendency to occupy covalently bonded tetrahedral network positions.^{41,42} In order to incorporate lead as $[\text{PbO}_{4/2}]^{2-}$ units in to the network, $[\text{POO}_{3/2}]$ units readily share the unshared corner resulting in $[\text{PbO}_{4/2}]^{2-} \cdot 2[\text{PO}_{4/2}]^+$ complexes. Once the $[\text{POO}_{3/2}]$ to $[\text{PO}_{4/2}]^+$ conversion is exhausted for want of $[\text{POO}_{3/2}]$ units, further addition of PbO begins to play the role of a modifier oxide like K_2O . Thus, in the presence of modifier PbO Mo^{5+} has little tendency to stabilize and the concentration of Mo^{5+} becomes low. These features are confirmed from ESR⁴¹ and ultrasonic⁴³ investigations (Fig. 3). In all their structural and important physical properties, phosphotungstate glasses are very similar to phospho-molybdate glasses.⁴¹

LEAD OXYHALIDE GLASSES

Lead oxyhalides are again among novel glass systems^{43,47} where the structure is built of $[\text{PbO}_2\text{X}_4]$ ($\text{X} = \text{F}, \text{Cl}$) octahedral units.⁴⁸ The components of these glasses

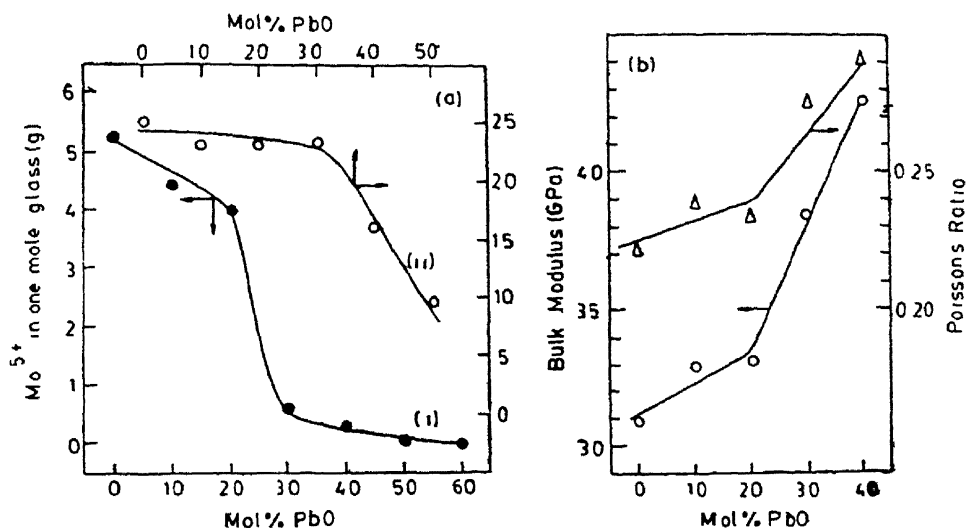


FIG 3 Mo⁶⁺ concentrations in lead phosphomolybdate glasses (a) variation of Mo in (i) (80-x) MoO₃-x PbO-20P₂O₅ glasses (ii) in (60-x) MoO₃-x PbO-40P₂O₅ glasses, sharp drop occurs in Mo⁵⁺ concentration as soon as concentration of PbO and P₂O₅ become equal, (b) variation of bulk modulus and Poisson's ratio in (80-x) MoO₃-x PbO-20P₂O₅ glasses. Here again trends in variation of elastic properties change when PbO concentration becomes equal to the concentration of P₂O₅ (see text).

namely PbO and PbX₂ (PbF₂ or PbCl₂) are known to be typical examples of covalently and ionically bonded solids respectively⁴⁹. While PbO and PbX₂ are themselves not good glass-formers, glasses containing 40–90 per cent PbO may be conveniently prepared. The halide rich glass compositions are characterized by high degree of ionicity. Presence of [PbO₂X₄] octahedral motif in all glasses was first postulated to account for the pair distribution functions obtained from X-ray diffraction measurements and were subsequently confirmed from detailed EXAFS investigation of the glasses^{46,50}.

Linkages of the type –O–Pb–O– form networks whose dimensionality and extent are reduced in halide-rich glasses in which O/Pb ratio decreases considerably. It is interesting to note that glass formation ceases in compositions where the linkages do not extend beyond –Pb–O–Pb–. The bond angle OPbO which is close to 90° in oxide-rich glasses as a consequence of *p*-orbital bonding of Pb to oxygen atoms gradually opens up as the ionicity increases in halide-rich glasses and the overall symmetry of [PbO₂X₄] units evolve from C_s → C_{2v} → D_{4h} as the halide concentration in the glass increases. These features have been confirmed from an analysis of X-ray absorption near edge structures (XANES) associated with Pb–L-edges (L₁, L₂ and L₃) in glasses (Fig 4)⁵¹. The nature of bonding in [PbO₂X₄] units can be understood in terms of suitable molecular orbital diagrams which involve the 6*d*-orbitals of Pb.

The nature of bonding in PbO–PbX₂ glasses is affected by the application of pressure on the glass⁴¹. In fact, crystallization occurs under pressure in both PbO–PbCl₂ and PbO–PbF₂ glasses in which Pb–O bond appears to get modified.

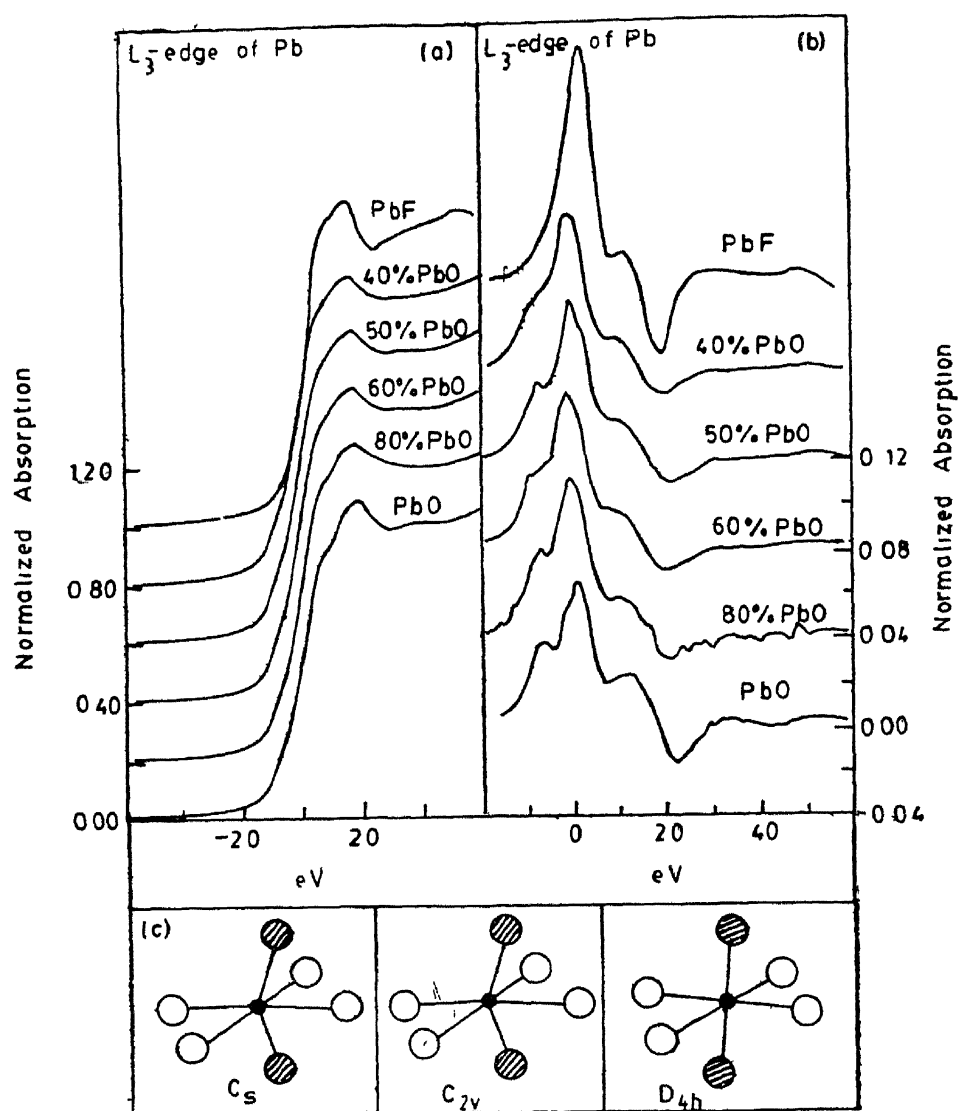


FIG 4 Bonding and structure of $[\text{PbO}_2\text{F}_4]$ units in PbO-PbF_2 glasses (a) X-ray absorption near edge structure (XANES) of PbO-PbF_2 glasses along with those of PbF_2 , (b) differentiated spectra corresponding to those in (a) in which absorption peaks are more clearly defined (c) The structural units whose MO diagrams were found account for the features in the spectra

leading to formation of O^{2-} ions. In oxychloride glasses in particular rearrangement into a crystalline product is assisted by formation of O^{2-} ions.

Hence, the structural aspects of molybdo phosphates and lead oxyhalide glasses provide evidence for the prevalence of octahedral motifs in and compatibility with the glassy state. Octahedral geometries seem to occur wherever d -orbital participation becomes energetically feasible.

COVALENCY AND GLASSY STATE

One of the traditional beliefs in glass science has been that good glass formers are highly covalently bonded⁵². The attributes of covalent-bonding are directionality

of bonding and shortness of the range of interaction (ideally confined to the connected pair). Both these features are considered to be factors contributing to facile elimination of long-range order necessary for glass formation. However, fully covalently bonded elements like silicon and carbon do not form glasses. It appears to us that the flatness of the $-M-O-$ or $-M-C-M-$ bond flexing potential is responsible in a major way for easy glass formation. Oxygen and chalcogens possess certain unique properties which may contribute to the glass-forming tendency, reasonably high electronegativity, and presence of lone pairs which can be engaged in additional bonding in extreme situations etc. It is also apparent that sixth group elements are unique in and dominate the glass chemistry.

Nevertheless, $M-O$ bonds in glasses in general appear to become more covalent in glassy state than they are in the corresponding crystalline state^{53,54}. This feature was first observed through chemical shifts in X-ray absorption edges.⁵⁵ The increase in covalency manifests quite generally as increase of edge absorption coefficients.^{45,51,56,57} The absorption edges correspond to excitations from core levels of the atoms to allowed vacant final states (atomic, molecular or band-like). The bonding details affect the transition dipole matrix element and thereby the absorption coefficient which is related to the square of the matrix element. Since increase in covalency may be considered as corresponding to reverse transfer of bonding electrons from the anion, these electrons affect the final states through enhanced shielding. Thus, intensity variations are quantitatively correlated to number of covalent electrons through shielding constants.⁵⁷ The extent of covalency itself may thus be quantified. In fact, it can be shown that the absorption coefficient μ_{cov} , of the covalently bonded atom and absorption coefficient μ_{ion} of the same in free ionic state are related as $\mu_{cov} = \mu_{ion} \exp [aS]$; where S is the shielding due to covalent electrons (involved in covalency) and a is a constant determined by connected quantum states in the free ion.

Investigation of L -edge spectra of Nd in NdF_3 - BeF_2 glasses,⁵⁶ of Th in ThF_4 - HfH_4 glasses⁴⁵ and of Pb in PbO - PbX_2 glasses⁵¹ have revealed that the bonding is always more covalent in glasses than in crystalline state. This is intriguing because increasing covalency generally leads to loss of total cohesive energy. But considering that glass has a lower density than the corresponding crystalline phase, loss of coulombic interactions is likely to be made up by a local enhancement of covalency.

PHYSICAL MODELS OF GLASSES AND THEIR LIMITATIONS

The two general physical models employed in the description of glasses are the random network model and the random close packing model. Random network model is generally considered adequate for describing covalent glasses such as fused quartz. Distribution in $Si-O-Si$ bond angles eliminates periodicity in glassy SiO_2 . The absence of such angle distributions induce an order characteristic of crystalline modifications like β -quartz. The distribution of bond angles is now well established through solid state high resolution magic-angle-spinning NMR

which has also been used to investigate structural species in modified silicate glasses ^{46a}

Random close packing on the other hand has been found to be particularly useful to model the structure of metallic glasses. Indeed, a close correspondence exists between random close packing and random network in that the interconnection of the tetrahedral voids of the rcp model generates a three-dimensional random network of tetrahedra.

From all the previous discussions it is obvious that ionic glasses cannot be described by either of these physical models without unduly severe modification. One could of course introduce artefacts of network decoration and attempt to use random network model to describe networks containing octahedra but once again it would underscore the necessity for more satisfactory structural models.

One serious question that such physical models do not address themselves to is, 'what is the origin of bond angle distribution itself?' The apparent reluctance of simple glasses such as fused quartz and B_2O_3 to crystallize even when a high degree of thermal energy is available suggests that the amorphous state with its frozen bond angle distribution is perhaps energetically not unfavourable. Whether there exists an inherent tendency to generate bond angle or bond length distributions does not form the subject matter of the physical models.

ACID-BASE CONCEPT AND CHEMICAL MODEL OF GLASSES

It is common chemical knowledge that all heteroatom bonds are characterized by mixed type of bonding, in particular ionic-covalent type in inorganic materials ⁵⁹⁻⁶¹ direction of the transfer of electron is from a cation to an anion or from a Lewis The acid to a Lewis base. Such bonding electron displacements are due to electronegativity differences. The acid-base concept is therefore rooted in the concept of electronegativity. The acid-base formalism is empirical and has been developed quite successfully. Parameterized values for acidity and basicity have been tabulated and a number chemical phenomena have been rationalized using such parameters.

One empirical measure of acidity of a cation is its bond valence corrected for the variation of the bond distance ⁶². The acidity or partial valence, s , and bond distance R are related as

$$s = \left(\frac{R}{R_0} \right)^{-N},$$

where R_0 and N are constants derived from analysis of crystal structure data from literally hundreds of compounds with a variety of coordination numbers. A large difference in the acidity of the cation and the basicity of the coordinating anion in a compound is an indication of the latter's reactivity or instability. Such a compound generally exhibits a tendency to acquire into its structure other atoms or groups of

atoms which ameliorate the imbalance in acid-base parameters. The imbalance can also be atoned by local distortions which alter the bond lengths in accordance with the above relation and increase or decrease the value of s . Thus a distortion would be introduced into the structure in order to atone differences in acid-base parameters wherever large differences exist. Such distortions would therefore reflect natural difficulty in crystalline packing or tendency for glass formation. Acid-base parameters of a few good glass-formers are presented in Table I below and it may be noted that the cation acidities are indeed quite different and much larger than the anion basicities.

TABLE I
Acid-base parameters of good glass formers

	acidity (a)	basicity (b)	(a/b)
SiO ₂	0.95	0.50	1.9
B ₂ O ₃	0.88	0.50	1.8
P ₂ O ₅	1.30	0.50	2.6
TeO ₂	1.06	0.50	2.12
ZnCl ₂	0.36	0.10	3.6
BeF ₂	0.50	0.21	2.4

One would, therefore, expect oxygen or other anions to displace themselves in such a way that the resulting bond distortions would increase their net valences. The acid-base model thus provides a reasonable explanation of inherent glass forming tendency in some materials. It would, therefore, be worthwhile examining this aspect further.

It would be equally profitable to ponder on the variations in electronegativities due to changes in hybridization of anions particularly oxygen. The different levels of s -mixing in the bonding orbitals of oxygen would not only introduce a distribution of bond angles but a distribution of bond electronegativities of oxygen atoms. The equilibrium cation-oxygen distances (the corresponding bond strengths) (due to different ionicities) would, therefore, again acquire a distribution in accordance with the principle of electronegativity equalization in the formation of chemical bonds. This would also contribute to an inherent glass-forming tendency because of the resulting basic symmetry in local configurations.

CONCLUSION

An attempt has been made in this presentation to show that structure stability and several properties of glasses are intimately connected to the nature of chemical bonds in them. Physical theories in their search for unifying models tend to underestimate, if not ignore, the bonding aspects. Models based on chemical approaches with their strong empirical base may therefore be expected to provide new and profitable insights.

ACKNOWLEDGEMENTS

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CHEMICAL COMPOSITION AND MAGNETIC INTERACTIONS IN AMORPHOUS TRANSITION METAL-METALLOID ALLOYS

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A study of magnetic interactions in the amorphous transition metal-metalloids is of considerable interest. Magnetic moments of the metal atoms in these systems lie close to the values found in analogous crystalline systems and like the latter follow the trend according to the Slater-Pauling curve. But the extent of charge-transfer from the metalloid to the metal atoms needs further investigations. In certain cases, the magnetic properties of these systems strikingly differ from the crystalline systems of similar compositions due to the presence of chemical environment of multiple types. The Curie temperatures (T_c) of these metalloids, unlike the crystalline systems, are significantly influenced by thermal history. However, like the crystalline systems they follow the Bethe-Slater relationship as a function of the radius of the d -shell of the transition metal ion. Structural disorder, in general, results in the lowering of T_c compared to the crystalline systems.

Mössbauer studies of iron-rich systems are characterised by the relative intensities of the hyperfine spectra and exhibit large line-widths due to the random distribution of the atoms. The plots of reduced hyperfine field vs reduced temperature show significant deviations from crystalline behaviour. Attempts to obtain detailed magnetic phase-diagrams using different techniques show the existence of spin-glass in addition to para- and ferro-magnetic phases. Not much study has been carried out on the reversibility of the different transitions. Variations in the critical compositions may be explained on the basis of competing interactions. Distribution in the interatomic distances also influence the critical concentration due to their effect on the exchange interactions. The critical exponents except β are found to be close to values predicted for the three-dimensional Heisenberg model.

Although these systems are amorphous they show the existence of spin-waves. Compared to crystalline systems these systems show $T^{3/2}$ dependence over a wider range of temperature. The values of stiffness constants indicate that spin-waves in amorphous ferro-magnets have lower energies of excitation and a description of localised spins with short range interactions is more appropriate. Attempts to apply the itinerant electron model do show the Arrot-Belov-Kouvel (ABK) plots to be linear. They however exhibit curvatures at low fields which is attributed to concentration fluctuations in these amorphous ferromagnets. The different aspects of magnetic interaction mentioned are discussed in some detail in the light of recent literature.

Key Words Magnetic Interactions; Amorphous; Transition Metal-Metalloids, Mossbauer Effect; Curie Temperatures; Bethe-Slater Relationship; Spin-Glass; Paramagnetic-Ferromagnetic Phases, Heisenberg Model; Arrot-Belov-Kouvel (ABK) Plots

INTRODUCTION

THE growth of interest on the subject of amorphous alloys in the last decade is indeed phenomenal. The explosive literature on the subject is partly governed by the search for new materials with potential technological applications and partly by the scientific curiosity to look for and understand unusual structural situations such as those obtained in amorphous materials. The reader may refer to any of the books that have appeared very recently for a comprehensive treatment of different aspects of the subject of amorphous materials.¹⁻⁵ Gubanov⁶ theoretically foresaw the existence of ferromagnetism in amorphous solids in 1960. Around the same time, the advent of amorphous ferromagnets began as a laboratory curiosity with the investigations of Duwez⁷ and co-workers and now has become a subject of industrial curiosity, attracting more and more workers from different fields into its fold. The present title is chosen for the review keeping in mind that magnetism in itself is quite an interesting field and this property in amorphous materials is likely to continue to be of considerable concern for quite sometime to come both from theoretical as well as experimental points of view. The subject matter has been sub-divided into different sections purely for the convenience of presentation and in a way reflect the patterns of literature on the subject of magnetism in general.

MAGNETIC MOMENTS OF TRANSITION METAL ATOMS IN TRANSITION
METAL-METALLOIDS

Amorphous magnetic alloys, prepared by various techniques⁴ possess a chemical composition T_xG_{1-x} with $x \approx 0.8$. Here $T = \text{Fe, Co or Ni}$ or a combination of these 3d elements, or a combination of them with other 3d elements such as V, Cr or Mn; G represents metalloids from group III A like B, IVA, such as C, Ge, Si, Sn or Va like P or more often a combination of these elements. The average magnetic moment, μ , per transition metal atom for various alloy compositions is listed in Table I.² These values have been obtained from bulk saturation magnetisation measurements utilising a force balance method or vibration magnetometer. The data clearly show that the presence of metalloid atoms decreases the value of μ relative to the values for pure transition metals, $2.2\mu_B$ for Fe, $1.7\mu_B$ for Co and $0.6\mu_B$ for Ni. This is a feature common for amorphous and crystalline alloys. For instance $\mu = 1.91\mu_B$ for Fe_2B and the reduction is attributed to charge-transfer from B to Fe. The differences in the reduction in alloys containing varying amounts of different metalloid atoms are attributed to the amount of charge-transfer from the metalloid atom which in turn is governed by the number of s-p electrons on the metalloid. Several attempts have been made to formulate simple rules that govern the observed trends. The use of generalised Slater-Pauling model by Mizoguchi *et al.*⁸ in the amorphous magnets with composition $(\text{Fe}_x\text{TM}_{1-x})_{80}\text{P}_{10}\text{B}_{10}$ ($\text{TM} = \text{Ni, Co, Mn, Cr, V}$), showed several features with trends similar to those in crystalline alloys. The Slater-Pauling curve obtained by plotting magnetic moment per TM atom vs the number N of TM outer electrons showed a maximum toward the lower value of N as in transition metal borides (Fig. 1). A distinguishing feature

TABLE I

Average magnetic moment, μ per transition metal atom in various transition metal-metalloids
(Ref. 2, p. 92 and references therein)

Alloy Composition	$\mu(\mu_B)$
$\text{Fe}_{80}\text{P}_{20}$	2.1
$\text{Fe}_{80}\text{B}_{20}$	1.94
$\text{Fe}_{80}\text{P}_{14}\text{B}_6$	1.85
$\text{Fe}_{70}\text{Ni}_{10}\text{B}_{20}$	1.86
$\text{Fe}_{70}\text{Ni}_{10}\text{P}_{14}\text{B}_6$	1.64
$\text{Fe}_{60}\text{Ni}_{20}\text{B}_{20}$	1.69
$\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$	1.31
$\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$	1.23
$\text{Fe}_{40}\text{Co}_{40}\text{B}_{20}$	1.79
$\text{Co}_{80}\text{B}_{20}$	1.28
$\text{Co}_{78}\text{P}_{22}$	1.18
$\text{Ni}_{80}\text{P}_{20}$	0.05

is a shift of the maximum to lower values of N in amorphous compared to crystalline systems with $\Delta N = 0.3$. Otherwise, the same linear decrease of the moment between iron and nickel is observed. Luborsky,⁹ from these trends concluded that roughly boron atoms transfer a charge of about one electron and phosphorous two electrons to the transition metal atoms. Such a prediction would mean that even variation of metalloid concentrations in systems such as $\text{Fe}_{40}\text{Ni}_{40}(\text{P}, \text{B})_{20}$ should

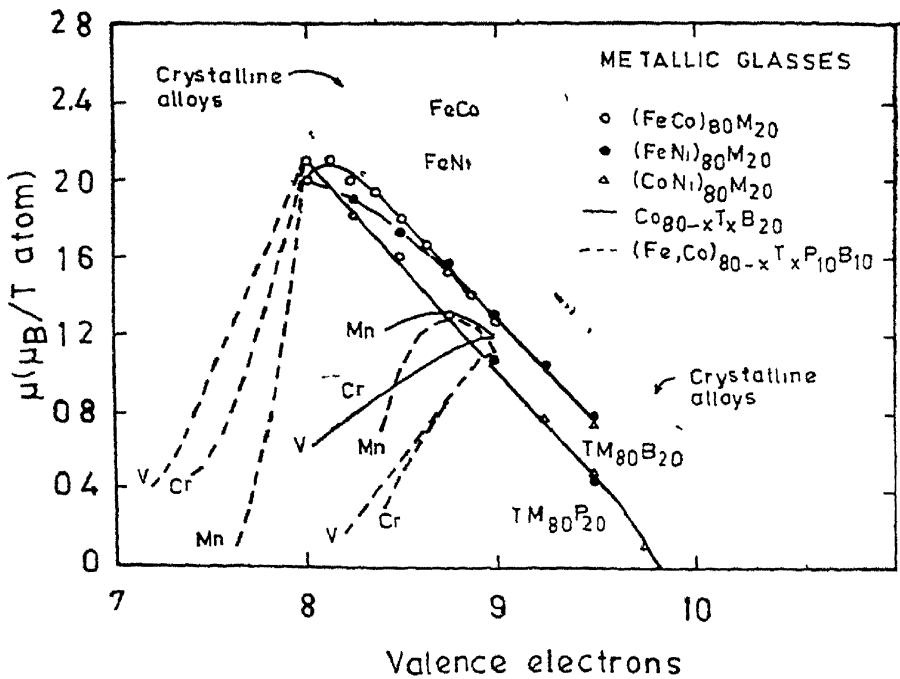


FIG 1 Dependence of mean saturation moment per transition metal atom on average transition metal valence electron concentration ⁸

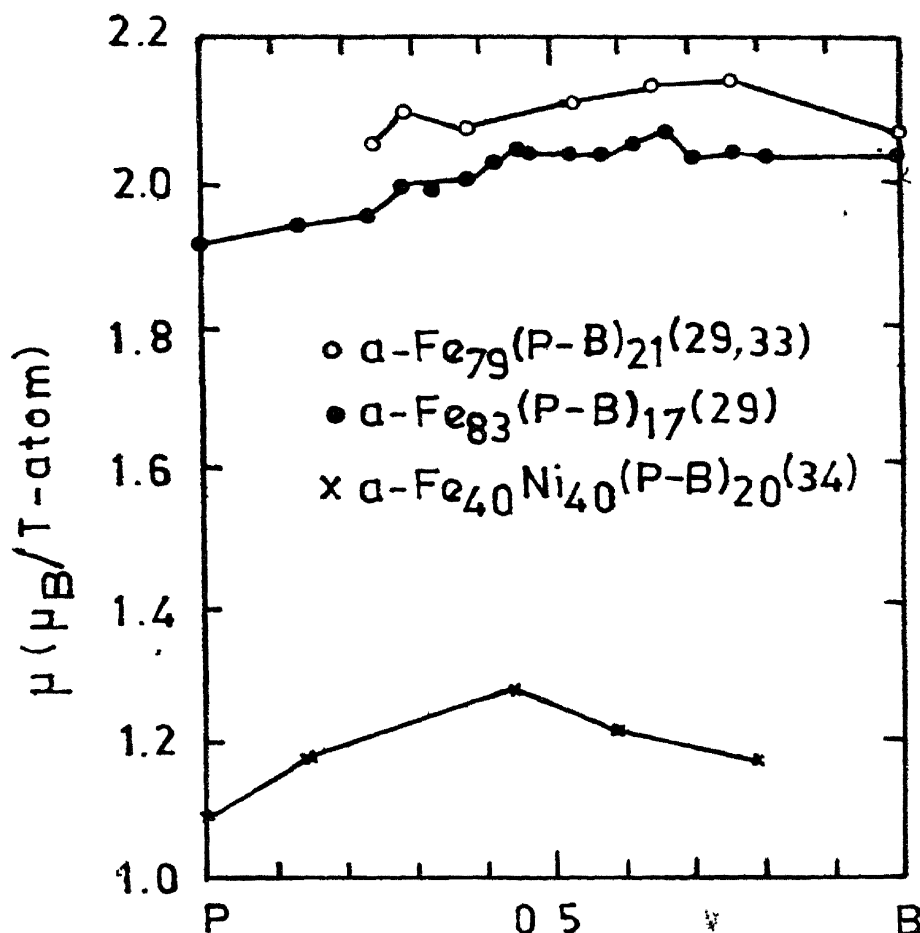


FIG 2 Changes in the average magnetic moment in α -transition metal-metalloid alloys with relative concentrations of P and B atoms ¹⁰

show a monotonic decreasing trend as P is replaced by B. This is not, however, found to be the case as shown in Fig 2.¹⁰ Thus it is difficult to account for details of moment variation in a simple manner. The above example suggests the importance of other aspects which can significantly influence the variation of magnetic moment with composition such as chemical bonding. It should at the same time be stressed that chemical bonding in amorphous alloys can be more difficult to handle than in crystalline systems. This may be highlighted, for example, by the observation that $\alpha\text{-Fe}_{0.5}\text{Si}_{0.5}$ and $\alpha\text{-Co}_{0.5}\text{Sn}_{0.5}$ are magnetic whereas the corresponding crystalline systems are non-magnetic ^{11,12}. Thus, amorphous systems can give rise to chemical environments of multiple type favouring existence of a magnetic moment.

Considerable work has also been reported on ternary alloys with no agreement regarding the moment to be associated with different transition metal atoms ¹³. Mizoguchi *et al* ⁸ concluded from the results on the alloys $\alpha\text{-(Fe, M)}_{30}\text{P}_{10}\text{B}_{10}$ mentioned earlier that Fe, Co and Ni possess approximate magnetic moments 2, 1 and $0\mu_B$ per atom respectively. A similar result is obtained by Sherwood¹⁴ on $\alpha\text{-(Fe, Co, Ni)}_{75}\text{P}_{16}\text{B}_6\text{Al}_3$. Yamauchi and Mizoguchi¹⁵ on a study of ternary alloys with a

single *TM* element found μ_{Fe} and μ_{Co} when taken equal to 2.6 and 1.6 μ_B respectively, the magnetic data agree reasonably well with values obtained using the rigid band model. Durand¹⁶ on the other hand concludes in the investigation of $a\text{-(Fe}_x\text{Ni}_{100-x})_{75}\text{P}_{13}\text{B}_8$ series that the moment per Ni atom increases steeply from zero at $x = 0$ to roughly a constant value of 0.4 μ_B for $x \geq 30$ at per cent. O'Handley *et al*¹⁷ have shown from a rigid band model analysis that Ni should have a non-zero moment in amorphous $\text{Ni}_{80}\text{B}_{20}$ alloy and B and P metalloid atoms donate 1.6 and 2.4 electrons per atom respectively to the *d*-bands of the *TM* atom. In a comprehensive study of the Fe-P-B alloys, Durand and Yung¹⁸ are able to account for the rate of reduction of iron moment when one metalloid is retained at constant percentage and the other substituted for iron, using a charge transfer model assuming B and P donate 1.4 and 1.6 electrons respectively to the Fe-*d* bands. The later value for P is significantly different from the one derived by O'Handley¹⁷ mentioned earlier. Kaul¹³ has rationalised the differing observations stated above by putting forth the idea that not only the moments of Ni and Fe atoms vary with Fe concentration as revealed by neutron diffraction in crystalline alloys, but also the number of electrons donated by the metalloid atoms to the transition metal *d*-bands. Such a hypothesis has been justified on the basis of the coherent potential approximations.^{19,20}

CURIE TEMPERATURES

The curie temperatures of amorphous alloys are of much greater interest than of crystalline metals for (1) they are influenced by composition due to the moment of the constituting elements, (2) by structural disorder (3) chemical bonding of the metalloids with the *TM* which cannot be understood in a simple way as in crystalline systems for reasons mentioned earlier. We discuss below the dependence of T_c on these different factors and briefly mention the different arguments and models proposed to explain the observations. T_c for amorphous nickel has been determined to be 540 K which is about 15 per cent lower than the crystalline Ni.²¹ Extrapolated estimate of T_c for amorphous iron from a study of $a\text{-FeZr}$ alloy leads practically to 0 K.²² Cobalt-based amorphous alloys have the characteristic property of having $T_c > T_x$ where T_x is the crystallisation temperature as shown for instance by a comparison of the Mossbauer spectra recorded with increasing temperature.²³ That Co based alloys indeed differ in their behaviour from Fe based alloys can also be illustrated with the cases of $a\text{-Co}_x\text{P}_{1-x}$ and $a\text{-Fe}_x\text{P}_{1-x}$ systems.^{18,24} With increasing x , T_c increases for the cobalt alloy leading to an extrapolated value of 1400 K for $x = 1$ unlike in $a\text{-(Fe-P-B)}$ alloy which shows a decrease with increasing x leading to T_c of 340 K for $x = 1$. This may be understood as due to the presence of Fe-Fe pairs that interact antiferromagnetically depressing the curie temperature.

Since the first approach by Gubanov,⁶ reduction in T_c by structural disorder has been envisaged by theoretical analysis by various workers.²⁵⁻²⁷ In the light of these theories, when the lowering of T_c from crystalline systems is of the order of

10 to 15 per cent, the influence of structural disorder can easily be understood as due to the smaller density (~ 3 per cent) in the amorphous state affecting the exchange integral in a molecular field model. A small but significant lowering of T_c in amorphous to crystalline systems has been observed in cases such as α -Fe₇₅P₆B₁₉, α -Fe₃B and α -Fe₃P^{18,28,29}. But when a drastic effect occurs as in α -YFe₂, the differences cannot be accounted for without going through a detailed band structure calculation. Comparatively, only a few calculations have been made to account for T_c variations with composition using the itinerant magnetism model^{30,31}. The direct exchange interaction in amorphous magnets may be given by the semiempirical Bethe-Slater curves as a function of the radius of d -shell, R_d and of the atomic separation, R . Chen *et al.*³² have thus shown that when T_c values of different glasses are plotted against R/R_d , the influence of metalloid addition and alloying among the transition metals on T_c can be qualitatively accounted for. The T_c dependence on composition in the alloys (Fe_xNi_{1-x})₈₀B₂₀, (Fe_xNi_{1-x})₈₀B₁₉Si₁₁ and (Fe_xNi_{1-x})₈₀P₁₄B₆ has been well accounted for in terms of the relationships between near neighbour exchange interaction and x put forward by Foo and Wu using the coherent potential approximation for disordered ferromagnetic binary alloys.^{13,33}

The T_c values measured by magnetic measurements are found to be significantly lower than values obtained by Mossbauer measurements which monitors the hyperfine field at a microlevel. This is a trend that has been observed in crystalline systems as well and is attributed to relaxation effects which the Mössbauer probe experiences close to T_c and is governed by the relaxation times. Yet another property which distinguishes amorphous magnets is the influence of thermal history on the curie temperatures which can be pronounced in some of these alloys. For example, in the case of Fe₇₈B₉Si₃ the T_c shifts to lower values with higher rate of heating as sensed by differential scanning calorimetry³⁴. Similar thermal effects on T_c observed for α -Ni-rich Fe—Ni—B glass by Davies and Grogan³⁵ has been attributed to structural relaxation effects associated with the diffusion of boron atoms³⁵.

MOSSBAUER SPECTROSCOPIC MEASUREMENTS

Mossbauer spectroscopic measurements have provided insight into magnetic properties in those systems which contain suitable isotopes such as ⁵⁷Fe, ¹⁰¹Dy etc., which act as Mossbauer probes³⁶. With this technique it is possible to have access to informations which are not otherwise possible as it has the advantage of probing at the microlevel and of monitoring the magnetic phenomena with associated hyperfine interactions. The Mossbauer profiles of a number of iron rich ferromagnetic glassy alloys reported are similar. They all exhibit a well-resolved six-finger pattern with relative intensities close to 3 4 1 1 4 3 compared to 3 2 1 1 2 3 observed for iron foil and many crystalline alloys³⁷⁻⁴². The spectral line-widths also are significantly broader. We reproduce in Fig. 3 the Mossbauer spectra of Fe₇₂Ni₁₈Mo₂B₁₆Si₃ over the temperature 80 to 750 K range as a representative example⁴³. The transformation from ferro- to para-magnetic state above T_c is

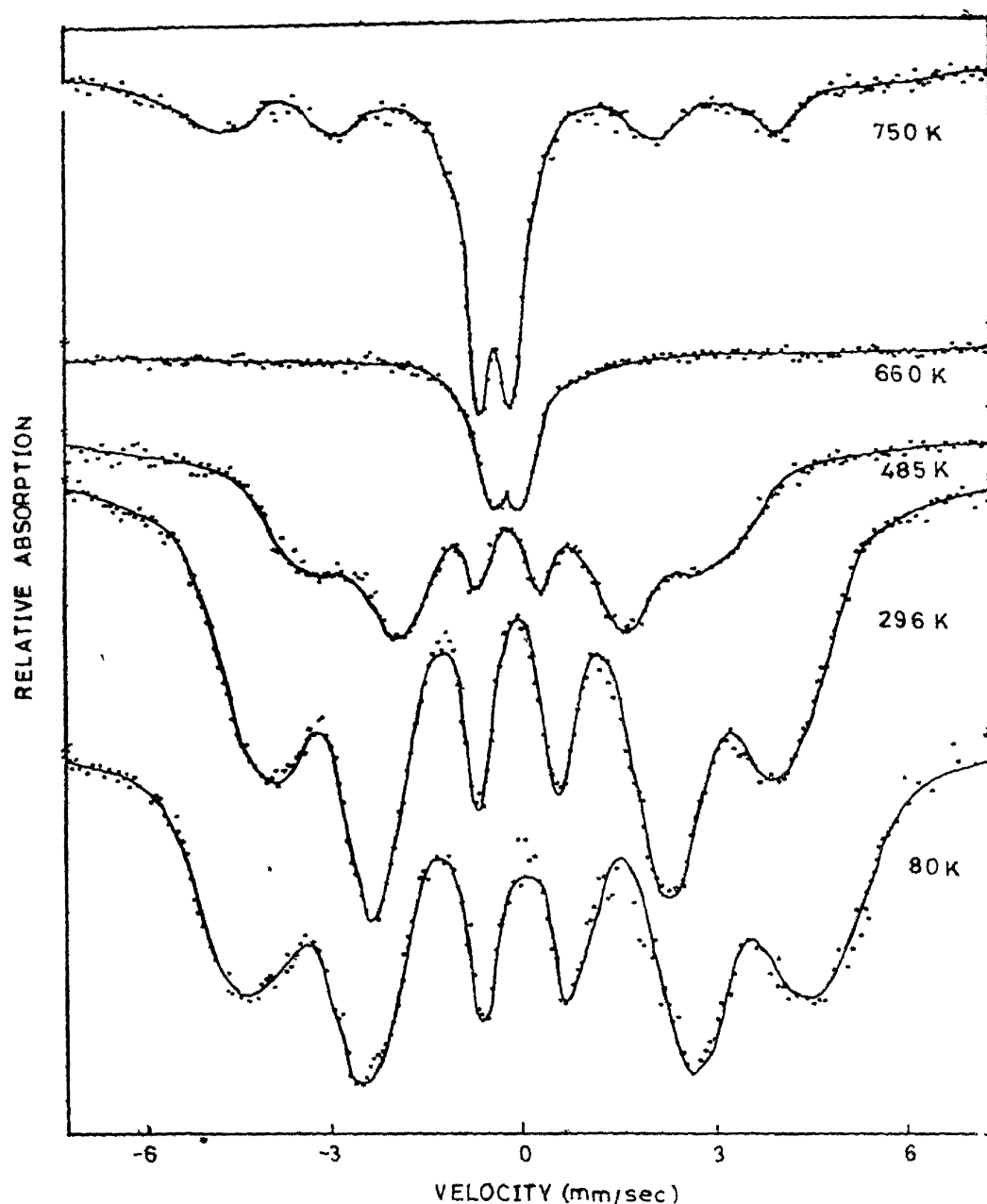


FIG 3 Mossbauer spectra of $a\text{-Fe}_{72}\text{Ni}_{15}\text{Mo}_2\text{B}_{16}\text{Si}_2$ between 80 and 750 K ⁴³

shown by a change from a six-finger pattern to a quadrupole split doublet. As a typical example, we give the least square fit experimental parameters, viz., line positions, line-widths and relative peak-areas obtained for the room temperature Mossbauer spectrum in Table II ⁴³. The large line-widths quoted should be compared with a value of 0.28 mm/sec obtained for the experimental line-width for natural iron. The characteristically broad lines with a symmetric profile uniformly observed in all the magnetic amorphous alloys arise due to iron atoms finding themselves in a variety of coordinations with random distribution of electric field gradient, which is significant as shown by the quadrupole-split paramagnetic spectra above T_c and which below T_c adds to the spectral line-widths without shifting the

TABLE II

Line-position, line-width and peak-areas of the Mossbauer spectrum⁴³ of α -Fe₇₂Ni₁₈Mo₄B₁₆Si₂

	Mossbauer lines					
	I	II	III	IV	V	VI
Line position (mm/sec)	-4.144	-2.347	-0.684	+0.496	+2.139	+3.898
(FWHM) (mm/sec)	1.758	1.283	0.537	0.671	1.534	1.714
Peak area (arbitrary units $\times 10^6$)	1.368	1.426	0.386	0.430	1.599	1.263

line positions. A survey of literature shows that extensive analysis of Mossbauer spectra of amorphous alloys throw light on the following aspects.³⁶ (1) Temperature-dependence of magnetisation (2) Distribution of hyperfine field and its temperature dependence and (3) Phase-transformations and associated phenomena. An attempt is made in this section to highlight these features as observed in the so-called metallic glasses.

The major handle that has been found to be of considerable value is the measurement of the hyperfine-field as given by the splitting of the spectra due to the internal magnetic field. The relative intensities of the six-finger pattern depends on the orientation of the magnetic field relative to the electric field gradient in the principal axes system.⁴⁴ Thus, the significantly different relative intensities in amorphous alloys compared to that in natural iron arises due to the fact that although the hyperfine field has a distribution, the components are predominantly oriented alike and in these cases along an axis perpendicular to the ribbon plane or close to such a description.⁴⁵ The magnitude of the hyperfine field depends on the contributions due to the Fermi-contact interaction, the dipolar and orbital contribution. At room temperature the amorphous alloys exhibit hyperfine-fields close to ~ 270 kOe which is significantly less than the value for natural iron viz. 330 kOe. This clearly shows that bonding between the metalloid atoms and the metal atoms in these alloys is quite important. It has been experimentally shown for these ferromagnets that the average hyperfine field is proportional to the bulk magnetisation with the proportionality constant being ~ 135 kOe/ μ_B where μ_B is the Bohr magneton. Fig. 4 shows a plot of the reduced magnetic field against reduced temperature for a few metallic glasses in addition to the Brillouin function for $S = \frac{1}{2}$ for comparison as it describes the temperature dependence for many crystalline ferromagnets such as iron. It is seen that the temperature-dependence for amorphous alloys differ significantly from the crystalline alloys and gives rise to a 'flatter' curve compared to the Brillouin function for $S = \frac{1}{2}$. This is found to be quite characteristic of many of the amorphous alloys studied although the disordered alloys also show a similar trend but to a much lesser extent.⁴⁶ This behaviour can be explained on the Handrich's⁴⁷ model based on the effective molecular field approach according to which the Brillouin function can be written in the modified form

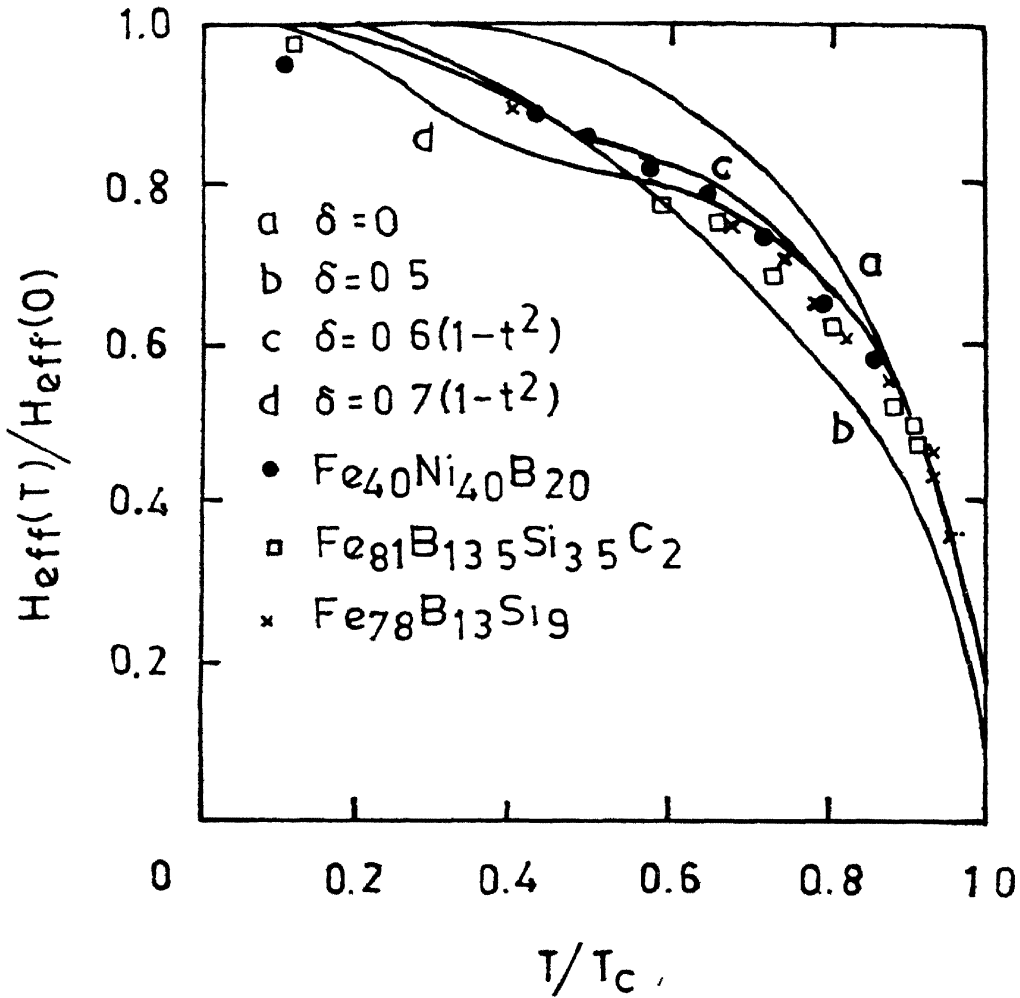


FIG 4 Reduced hyperfine magnetic fields vs reduced temperature—solid lines are drawn using eq (1) with different values of ∂ ³⁸

$$h = \frac{H_{\text{eff}}(T)}{H_{\text{eff}}(0)} = \frac{B_s[(1 + \partial)x]}{2} + \frac{B_s[(1 - \partial)x]}{2}, \quad (1)$$

where B_s is the Brillouin function for spin S , $x = [3S/S + 1] (h/t)$, $t = T/T_c$, and ∂ is a measure of the fluctuations occurring in the exchange interactions due to the random distribution of atoms in these solids and its value lies between zero and unity. For $\partial = 0$ expression (1) reduces to the form applicable to crystalline ferromagnets. It is found that in order to obtain a qualitative agreement with experimental points the values ∂ as high as 0.5 have to be used but even then quantitative agreement remains far from satisfactory. Prasad *et al* ^{36–39} showed that this agreement can be considerably improved if ∂ is assumed to have a temperature dependence, given by $\partial(t) = \partial_0(1 - t^2)$. Fig 4 shows that most of the experimental points lie on the theoretical lines assuming temperature dependence of ∂ of the above form with $\partial_0 = 0.6$ and 0.7. Subsequently, various authors have theoretically looked into the possible reasons for the temperature-dependence of magnetisation which cannot be explained fully on the Handrich's model. Fahnle⁴⁸ has

attempted the Monte Carlo simulations in disordered ferromagnets for a simple cubic lattice. Fig. 5 shows his results obtained for a finite lattice. The high temperature tails are found to depend on the lattice size but the low temperature data are found not to be influenced by lattice size considerations and reproduce the flattening behaviour observed experimentally. In these calculations consideration has been given both for the fluctuations of the exchange interactions (bond-disorder) as well as of the magnetic moments (site-disorder). Correlations between the exchange fluctuations (correlated bond-disorder) have been found to lead to enhanced flattening effect in the temperature dependence of reduced magnetisation. By way of rationalising the temperature-dependence observed by Prasad *et al*³⁶⁻³⁹ Kaneyoshi and Tamura⁴⁹ have considered the possibility of temperature-dependent distribution of magnetic moments. These authors have justified their approach on the ground that the line-widths of the Mossbauer spectra are found to decrease monotonically with temperature. However, it is found that the empirical expression suggested by Prasad *et al*³⁶⁻³⁹ gives a much better fit with experimental data than the expression of Kaneyoshi and Tamura particularly in the region $0.4 < T/T_c < 0.7$, where the deviation is maximum from the Brillouin function. This is attributed to the possible error in assuming a monotonic function for temperature, dependence of distribution

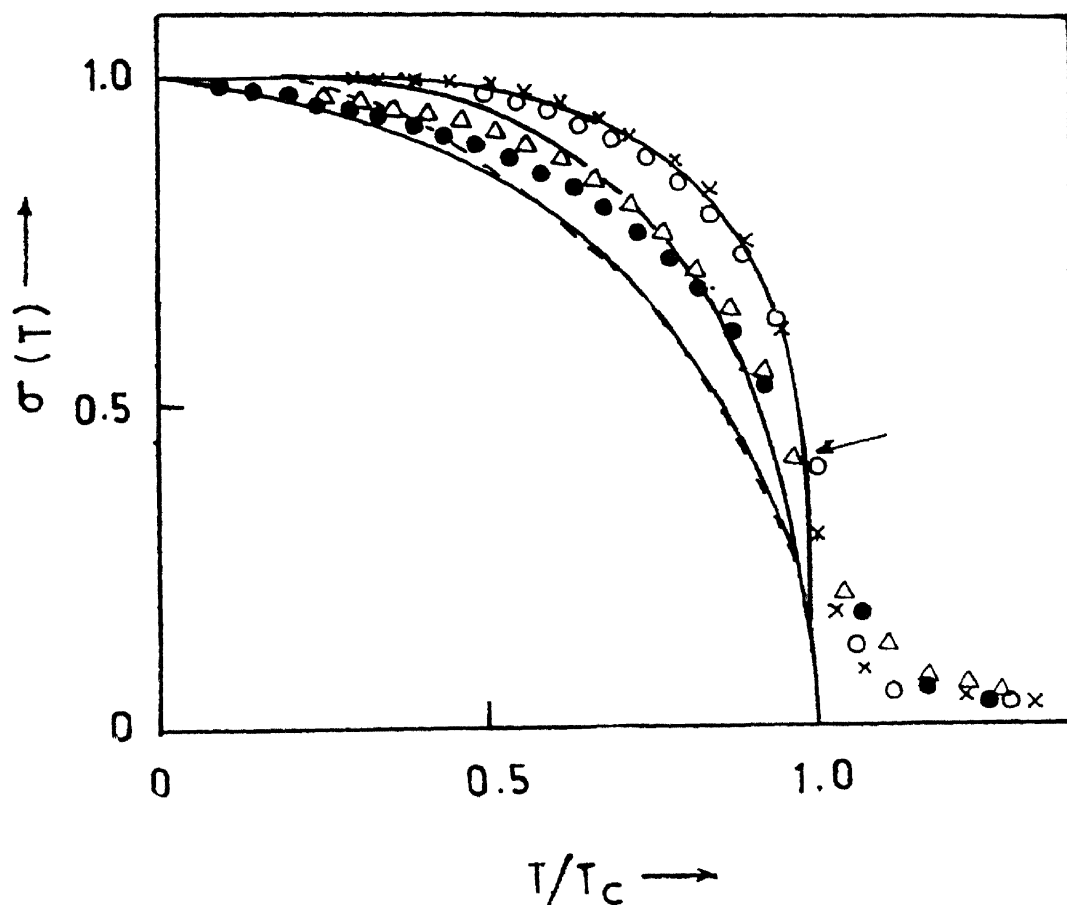


FIG. 5 Monte-Carlo simulations of temperature dependence of reduced saturation magnetisation (T) for crystalline, bond- and site-disordered cubic Ising systems and experimental data.

as evidenced for instance by a quadratic dependence of the line-width obtained by Narendra babu *et al.*⁴³ using a model-independent analysis of hyperfine-field as discussed below.

The broad and overlapping spectral lines in the Mossbauer spectra of metallic glasses are attributed to a hyperfine field distribution, $P(H)$, arising from a large number of non-equivalent sites. A number of methods have been developed to analyse the spectrum to obtain $P(H)$. The model independent approach due to Window is being widely used for this purpose and modifications for this procedure have been suggested⁵⁰⁻⁵². A representative result of $P(H)$ analysis obtained using Window's method for the amorphous alloy is reproduced in Fig 6. The results of such analyses lead to the following observations. The $P(H)$ curves obtained for most of the amorphous alloys are smooth, well-defined, structureless and usually exhibit a single maximum in the distribution. The oscillatory behaviour is an artefact due to the truncation of the Fourier series. The $P(H)$ curves are characterised by the parameters $H(P)$, the most probable field, ΔH half-width and $\bar{H}$, the average field. The significantly wide distribution in the hyperfine field in amorphous alloys may be appreciated from the fact that ΔH values have been found to be between 60 and 90kOe compared to ~ 43 kOe for disordered alloys.⁴⁶ The spread in the hyperfine field at room temperature is found to have a range for the value of the magnetic moment from $1.0 \mu_B$ to $2.65 \mu_B$, thus indicating that the range extends even beyond that of α -iron ($2.2 \mu_B$). The temperature-dependence of the average field and the maximum field show trends similar to those discussed in the earlier section. Mossbauer spectra clearly distinguish amorphous alloys which have magnetic inhomogeneity from those which do not. This may be well illustrated by the a typical Mossbauer spectra reported by Chien⁵³ for α -(Fe₃₂Ni₃₆Cr₁₄P₁₂B₆) reproduced in Fig. 7 which may be compared for example with Fig 2. In this case, the $P(H)$ distribution shows a pronounced asymmetric distribution with two significant peaks which has been attributed to two different types of near neighbour environment^{53,54}. The Mossbauer results pertaining to phase transformations are discussed in the ensuing sections.

MAGNETIC PHASE-DIAGRAMS

(a) Nature of the Phases and Comparison with Crystalline Systems

The nature of interaction between two 3d-impurity atoms such as Mn, Cr, Fe etc, in a non-magnetic host such as the noble metals like Cu, Ag or, Au has been shown to depend on the nature of the impurity atoms as well as those of the hosts. Concentration of the impurity atoms is the key factor in deciding the nature of the interactions. At very low concentration, e.g., < 50 ppm the interaction is very weak. This single impurity regime is referred to as the Kondo⁵⁵ regime. At very large concentrations, > 20 at per cent, the direct exchange interactions lead to an ordered magnetic state. In the intermediate concentration range, in the first phase between 0.1 and 10 at per cent, the impurities interact strongly enough through the RKKY⁵⁶ interaction but direct exchange forces are relatively unimportant. In this

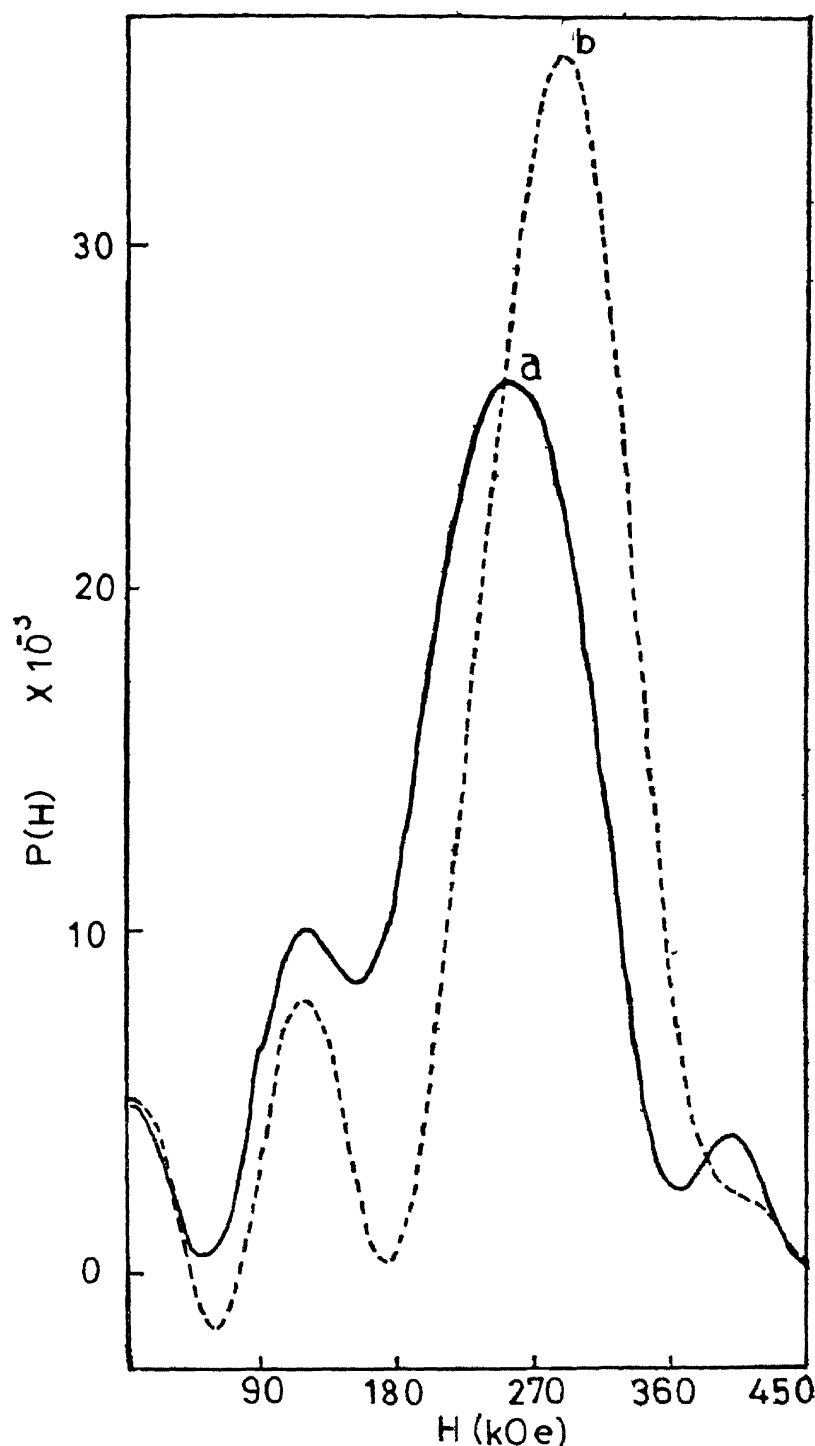


FIG 6 Distribution of hyperfine-field at 80 K for $a\text{-Fe}_7\text{Ni}_{10-x}\text{Mo}_x\text{B}_{16}\text{Si}_2$ alloys (a for $x = 6$, b for $x = 2$)⁴¹

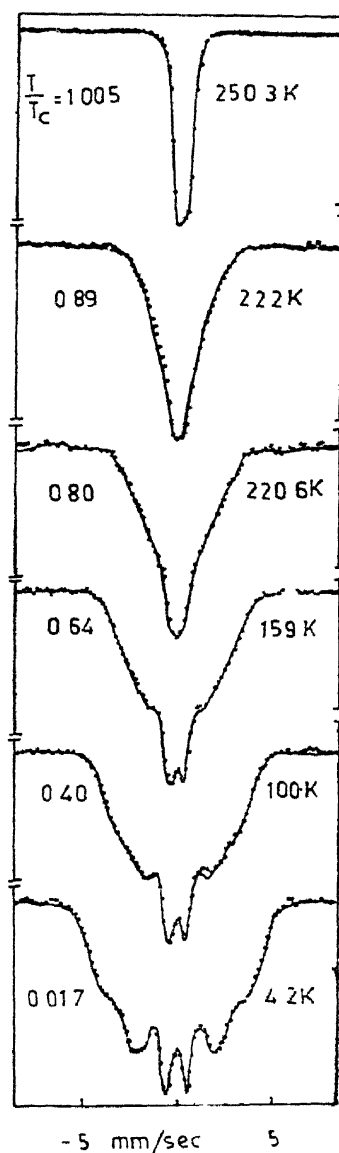


FIG 7 Mossbauer spectra of $a\text{-Fe}_{13}\text{Ni}_{36}\text{Cr}_{14}\text{P}_{12}\text{B}_6$ in the temperature range 4 to 260 K⁵¹

region, the RKKY-coupling can be both positive as well as negative due to the randomness in the distribution of the exchange interactions and is referred to as the spin-glass region. In the subsequent region with the impurity concentration ranging between 10 and 20 at per cent, the spin-glass situation coexists with the onset of

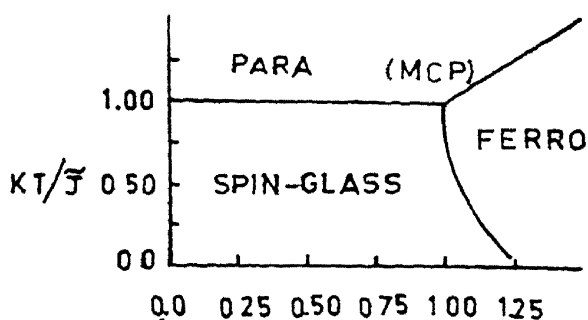


FIG 8 A schematic magnetic phase-diagram based on the model of Sherrington and Kirkpatrick⁵⁴

direct exchange and is variously referred to as 'cluster glass', micro-magnetism etc. Edwards and Anderson⁵⁷ were the first to suggest a lower magnetic state without long range order with randomly oriented spins leading to spin-glass behaviour. They proposed a ground state for the system whose order parameter is taken to be the spatial average of the square of the thermal average of the spins over a given configuration. Following this suggestion, Sherrington and Kirkpatrick⁵⁸ put forward a model in which the distribution of exchange energies are characterised by a mean value $\tilde{J}_0$, a measure of the ferromagnetic exchange coupling and $\tilde{J}$ the width of the pair exchange distribution $\tilde{J}_i$. Solution of this infinite range model leads to the phase diagram shown in Fig 8. Based on the type of interactions discussed above, there appear three phases, paramagnetic, ferromagnetic and spin-glass which meet at a multi-critical point (MCP).

The experimental realisation of magnetic phase diagrams with the above features should be considered to be less than quantitative particularly due to the absence of a clear-cut change over from one phase to another as a function of impurity concentrations. One of the most well-studied systems in these studies pertains to the magnetic phase diagram of Au-Fe alloys constructed from anomalies observed in various experimental results⁵⁹. In view of the range of interactions that come into question a number of experimental techniques such as ac and dc susceptibilities, specific heat measurements, muon spin resonance, ferromagnetic resonance, Mossbauer spectroscopy neutron scattering studies, Hall Effect etc., which have been earlier employed to obtain the magnetic phase diagrams for the study of impurity interactions between magnetic atoms at various concentrations in crystalline systems, have been brought into bearing in the investigation of amorphous magnets as well.⁶⁰⁻⁶⁶ Before discussing the results of these studies it may be stated that among the three phases in the phase diagram, spin-glass has attracted maximum attention. This term in literature is rather broadly used to refer to a region with competing interactions resulting in frustration. The frustration may occur in any type of materials that include magnetically dilute or concentrated, crystalline or amorphous, metallic or insulating. Recent works show the inherent difficulties in handling the spin glass problems theoretically as well and re-examine many concepts such as linear response theory, the concept of low-temperature phase having a lower free-energy compared to the phase at higher temperature etc.²

Fig 9 illustrates the typical phase diagrams obtained for amorphous alloys.⁶⁷ The phase-diagram shows a multicritical point with a critical concentration, a 'reentrant' transition as a function of temperature at relatively low temperature regions and a para to ferromagnetic and reverse transformation at higher temperatures. Based on these magnetic phase diagram investigations, the following observations may be made. The amorphous alloys permit study of spin-glass state over a wider region of concentration due to more favourable phase diagrams. The phase diagrams also show that in very dilute concentrations, the spin-freezing temperature, T_f , is proportional to the concentration of impurity atoms such as Fe, Co, or Mn. A nonlinear dependence appears beyond a particular concentration which is characteristic of the system in question. For instance the linear behaviour is observed in $\text{Fe}_x\text{Pd}_{30-x}\text{Si}_{20}$ even upto 7 at per cent compared to most other alloys such as $\text{Fe}_x\text{Ni}_{80-x}\text{P}_{12}\text{B}_8$ etc, where linearity is limited to much lower concentration of about only 2 at per cent^{16,64}. The slope of the curve indicating the para to ferromagnetic transformation by the change in T_c with composition is also characteristically different from system to system. Lack of knowledge about the transition from spin-glass to cluster glass-type interaction, magnetic inhomogeneity, etc, makes it difficult to discuss such trends in a definite manner.

(b) Critical Concentration

In an alloy of the type A_xB_{1-x} where B is non-magnetic, chemical disorder leads to percolation. At a critical concentration, x_p , many of the A atoms form bulk clusters. The remaining ones form isolated clusters. Thus above x_p , magnetic ordering sets in and long-range interactions are important. And below x_p , short-range interactions are important. x_p critically depends on the range of interaction and for the nearest neighbour coupling it is $2/N$ where N is the number of the nearest

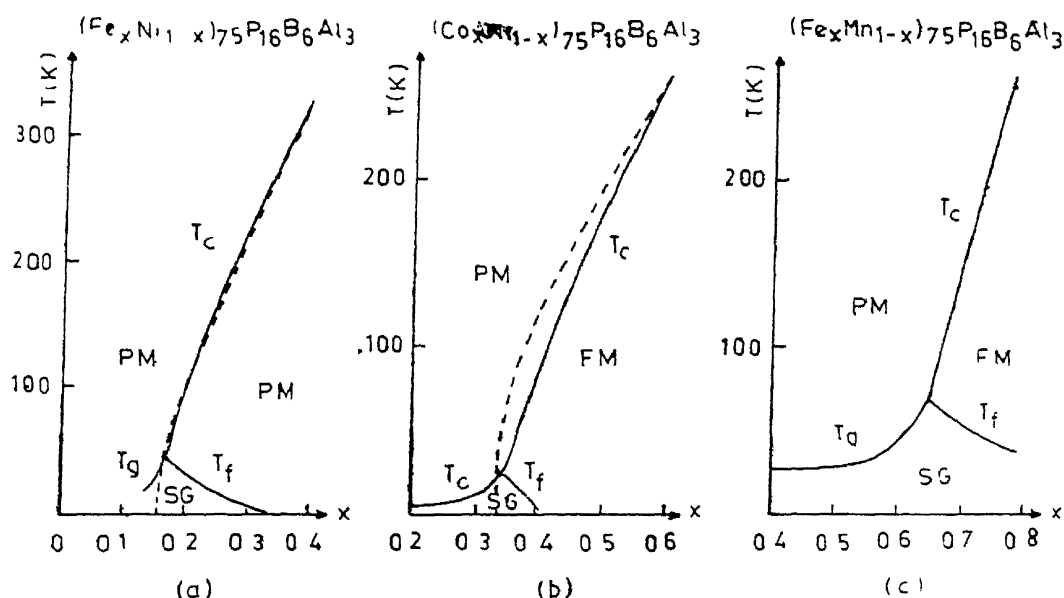


FIG 9 Phase diagrams for three series of $a-(A_xB_{1-x})P_{16}B_6Al_3$. Dashed lines are from theoretical models [(Ref 68) and references therein]

neighbours. In amorphous alloys assuming dense random packing N has a value between 10 and 12 giving $x_p = 0.2$ ⁶⁸. Experimentally observed x_p values significantly deviate from the above value for the following reasons. Most of the systems studied are ternary or quaternary systems. x_p as mentioned earlier depends on chemical and topological disorder and thus metalloid atoms can be expected to play an important role. The nature of the interactions between different transition metal atoms in these systems will also influence x_p . This is well brought out as shown by the phase diagrams of $(A_xB_{1-x})_{75}P_{16}B_6Al_3$, where (A, B) and (Fe, Ni), (Co, Ni) and (Fe, Mn) where the critical concentrations differ significantly (Fig 9). The critical concentrations reflect the differences between alloys with good moments such as Fe-Ni, alloys with discontinuous appearance of moments such as Ni-Co and Fe-Sn base alloys and alloys with competing interactions such as Fe-Mn, Fe-Cr and Co-Mn base alloys. The much higher critical concentration observed for Fe-Mn base alloys for instance, is attributed to the antiferromagnetic contribution by manganese.⁶⁹ In iron rich amorphous alloys, however, with a distribution of interatomic distance, due to the Fe-Fe interaction which significantly differs with interatomic distance, no simple explanation can be considered unequivocal.

(c) *Spin Glass Behaviour*

By way of illustrating how different experimental techniques may be employed in the study of magnetic interactions both from the point of interest of magnetism in amorphous materials as well as in spin-glass phase in general, discussion of some of the works reported in literature may be appropriate at this point. A temperature-dependent study of low-field magnetic susceptibility on magnetic glasses such as $\alpha-(Fe_xNi_{1-x})_{97}P_{13}B_8$ and $\alpha-(Fe_{0.2}Ni_{0.8})_{75}P_{16}B_6Al_3$ show sharp cusps similar to those found in well-established dilute spin-glasses, the maximum shifting to higher temperatures with increasing values of x .¹⁶ Temperature-dependence of magnetisation in the B alloys show broad maxima typical of reentrant phase transition.⁷⁰ Different theoretical models which either employ a phase transition approach or invoke a spin-freezing mechanism have been proposed to describe spin-glass behaviour.^{57,71} But no single theory fully explains all the experimental features. Recently, the frequency-dependence of ac susceptibility has been shown to be of value in ascertaining which of the theoretical descriptions, equilibrium or non-equilibrium phase transition metastable state or thermally activated phase change, is more appropriate.⁷² Such detailed investigations are relatively scarce in literature. Ferromagnetic resonance has been employed to study the reentrant behaviour in $\alpha-(Fe_xNi_{1-x})_{75}P_{16}B_6Al_3$ and $\alpha-Fe_xB_{100-x}$ alloys.^{61,66} In the iron-boron alloys, the onset of spin-glass behaviour is discerned by the observation that the FMR line-widths are independent of temperature above 130 K but show an increasing value as temperature is lowered, the increase being more significant, lower the iron content. The temperature dependence of resonance field has been found to be dependent on the heating or cooling rates lending credence to the suggestion that the spin-glass state is inherently non-ergodic.² The spin-glass transition in $\alpha-Fe_xSn_{100-x}$ has been studied by temperature variations in magnetization.⁷³ A reversible trend close to

T_c and an irreversible behaviour below T_f have been observed and the magnetic phase diagram obtained. It would be quite interesting to study this system by Mossbauer spectroscopy as both iron and tin sites can be examined by this technique.

CRITICAL BEHAVIOUR

The critical behaviour of amorphous transition metal-metalloids mainly pertains to ferromagnets. The detailed behaviour of systems undergoing a second order phase transition close to the Curie temperature where the ordered state appears has attracted great deal of attention in crystalline materials and attempts have been concentrated in the study and comparison of similar situations between crystalline and amorphous systems and within amorphous systems as well. Current approaches to critical phenomena pertain to the adherence to the static scaling hypothesis suggested by Domb, Hunter and Widom⁷⁴. It is based on the assumption that close to critical point the Gibb's potential or other equivalent thermodynamic potentials can be expressed as a homogeneous function of two variables, the reduced temperature $\epsilon = (T - T_c)/T_c$ and field conjugate to the order parameter. For a ferromagnet the order parameter is the magnetisation M and the conjugate field is the magnetic field H and near T_c as $H \rightarrow 0$, the equation of state may be written as

$$\frac{H}{|\epsilon|^{\beta+\gamma}} = f_{\pm} \frac{M}{|\epsilon|^{\beta}}, \quad (2)$$

where the $\pm$ refer to the sign of $|\epsilon|^{\beta}$ is the critical exponent describing the temperature-dependence of spontaneous magnetisation just below T_c with

$$M \sim (T_c - T)^{\beta}, (H = 0) \quad (3)$$

and γ is the critical exponent describing the temperature-dependence of susceptibility above T_c with

$$\lim_{H \rightarrow 0} \left(\frac{H}{M} \right) = x^{-1} \sim (T_c - T)^{\gamma} \quad (4)$$

Though the functional relation depends on the sign of the static scaling hypothesis expressed by eq (2) implies that the normalised quantities, $H|\epsilon|^{-(\beta+\gamma)}$ and $M|\epsilon|^{-\beta}$ are uniquely related though relate to situations both below and above T_c . Further, the hypothesis leads to a relationship of the critical exponents of the form

$$\beta + \gamma - \beta\vartheta = 0, \quad (5)$$

where ϑ is the exponent for the critical isotherm

$$M \sim H^{1/\vartheta} (T = T_c, H \rightarrow 0) \quad (6)$$

The scaling hypothesis was put on a firm theoretical ground by Wilson⁷⁵ using the renormalization group transformation. The methods and results of this approach have been reviewed. The theoretical values of the critical exponents have been

derived to be $\beta = 0.3647 \pm 0.0012$, $\gamma = 1.3866 \pm 0.0012$ and $\nu = 0.7054 \pm 0.0011$ for the three dimensional Heisenberg model⁷⁶ The soundness of the theoretical approach has been demonstrated by careful neutron scattering experiments and magnetic measurements on EuO and EuS which gave $\beta = 0.37 \pm 0.015$, $\gamma = 1.40 \pm 0.03$ and $\nu = 0.70 \pm 0.02$.⁷⁷ The transition metals Fe, Co, and Ni also exhibit critical exponents close to the theoretical values within experimental errors⁷⁸ The major cause of deviation from theoretical values is the existence of long-range interactions such as due to dipolar forces in real systems Kadanoff *et al*⁷⁹ have analysed the influence of these interactions and their analysis is helpful in estimating the critical region. Testing the applicability of the scaling hypothesis for amorphous ferromagnets is of great interest as a positive answer would imply that these amorphous alloys are magnetically isotropic on a microscopic scale and systems having a distribution of exchange interactions can indeed exhibit a second order phase transformation. The experimental determinations of critical exponents in these systems have been carried out using magnetisation data, Mossbauer spectroscopy and specific heat measurements The studies have to be naturally limited to systems which have curie temperature below crystallisation temperature. One of the early investigations in these lines is due to Mizoguchi *et al*⁸⁰ who showed the validity of the scaled magnetic equation of state for $a\text{-Co}_{70}\text{B}_{30}\text{P}_{10}$ Representative results for critical constants gathered from published literature as given in Table III. It is seen that the critical exponents except β , which shows noticeable deviation, exhibit values close to the ones predicted from the three-dimensional Heisenberg model and satisfy eq. (5) An idea about the extent of critical region may be obtained using the relationship due to Kadanoff *et al*⁷⁹ who have suggested that long-range interactions are negligible provided

$$|\epsilon| \gg \frac{g\mu_B S M(O)^{1/\beta(\delta-1)}}{kT_c} \equiv t_c, \quad (7)$$

where β and δ have the same significance as discussed earlier and the other terms have their usual significance In amorphous alloys the extent of critical region has been found to be significantly larger than in crystalline materials For instance, in $a\text{-Fe}_{10}\text{Ni}_{70}\text{B}_{19}\text{Si}_1$ in the critical region $|\epsilon| = 0.1$ for $T < T_c$ and $|\epsilon| = 0.08$ for $T > T_c$ the value of t_c is determined to be 2×10^{-3} compared to $|\epsilon| = 10^{-2}$ for crystalline materials.⁸¹ Yet another noteworthy feature that characterises the amorphous alloys is the higher value of β which is found to be close to 0.41 compared to 0.365 for a Heisenberg ferromagnet (Table III) Several reasons have been suggested for the higher values In the light of a Monte-Carlo analysis of a 20³ spin model with a 2³ bond cluster, Poon and Durand⁸² have suggested that the missing exchange bonds are responsible for the higher β values. The role of defects resulting in higher β is supported by the observation that for free surfaces β values as high as 0.75 are possible.⁸³ Within the amorphous ferromagnets, those containing more than one transition metal ions such as $a\text{-Fe}_{32}\text{Ni}_{36}\text{Cr}_{14}\text{P}_{12}\text{B}_8$ have been found to have higher values for the critical exponents In such cases, decomposition of the data on the basis of two environments has been found to lead to values in conformity with other amorphous alloys⁸⁴

TABLE III

Comparison of critical constant of amorphous ferromagnets and crystalline systems

	β	γ	a
α -Co ₇₀ B ₂₀ P ₁₀	0.402 ± 0.007	1.342 ± 0.025	4.39 ± 0.05 ⁸⁸
α -Fe ₈₉ P ₁₃ C ₇	0.38 ± 0.02	1.30 ± 0.05	4.47 ± 0.05 ^a
α -Fe ₂₀ Ni ₆₀ P ₁₄ B ₆	0.39 ± 0.02	1.33 ± 0.05	4.45 ± 0.07 ^b
α -Fe ₁₀ Ni ₇₀ B ₁₉ Si ₁	0.42 ± 0.02	1.35 ± 0.04	4.49 ± 0.04 ⁸¹
α -Fe ₃₂ Ni ₃₆ Cr ₁₄ P ₁₂ B ₈	0.43 ± 0.02	1.33 ± 0.05	4.43 ± 0.17 ⁸⁴
Iron	0.389	1.33	4.35 ⁷⁸
Nickel	0.378	1.34	4.58 ± 0.02 ⁷⁸

^aK Yamada Y Ishikawa Y Endo and T Masumoto *Solid State Commun* 16 (1975) 1335^bS N Kaul *Phys Rev* B23 (1981) 1205

SPIN-WAVE THEORY AND AMORPHOUS MAGNETS

Whether spin-waves exist under the structural condition of short-range order is of interest from the theoretical point of view since in amorphous materials with random distribution of atoms the so called "wave-vector" k is not a good quantum number and no simple description of Brillouin zone exists⁸⁵. Even before the advent of ferromagnetic metallic glasses, Herring and Kittel⁸⁶ from field theoretical arguments and Kaneyoshi⁸⁷ on a dense random packing of atomic spheres in these solids showed that spin-wave theory has a wider applicability than originally envisaged by the Heitler London-Heisenberg model. In the last decade large amount of data based on neutron scattering, low temperature magnetisation, Mossbauer and ferromagnetic resonance measurements have been gathered to demonstrate the existence of well defined long wave-length spin-wave excitations^{84,86-89,90}. They have been found to follow a normal ferromagnetic dispersion relation,

$$E_k = \Delta + Dk^2 + Ek^4 + \dots, \quad (8)$$

where $\Delta \ll Dk^2$ denotes an effective energy gap resulting from dipole-dipole interaction. At low temperatures, magnetisation, as in crystalline ferromagnets, follows the Heisenberg model relations,

$$\left[M(O) - \frac{M(T)}{M(O)} \right] = \frac{M(T)}{M(O)} = BT^{3/2} + CT^{5/2} + \dots, \quad (9)$$

where the symbols have their usual significance. Among the many experimental evidences available for spin-waves in these materials, those due to neutron scattering bring to light certain features which cannot be observed otherwise. Mook *et al.*⁹¹ have observed in a neutron-scattering study of α -CoP a "roton-like" structure with a minimum near the wave-vector Q corresponding to the first peak in the structure factor $a(k)$. Alben⁹² performed Monte Carlo calculations and attributed the results to static structural correlations. In neutron inelastic scattering experiments, certain peaks appear in addition to those which can be accounted for on the basis of spin-

wave excitations. These additional peaks have been attributed to a new type of elementary excitation as a result of the randomness of the structure and the term 'amorphions' has been introduced by Handrich⁹³. It has been shown that the dispersion of spin waves may have entirely different structures depending on the spatial dependence of exchange interaction⁵. Evidence for the same is obtained on the basis of neutron diffraction experiments. On the other hand, magnetisation and hyperfine field data from Mossbauer spectra lend themselves to straight-forward explanation on the basis of eq (9). The plot of $1 - H_{\text{eff}}(T)/H_{\text{eff}}(O)$ vs $T^{3/2}$ gives rise to linear relationship for $(\text{Fe}_x\text{Ni}_{1-x})_{75}\text{P}_{16}\text{B}_6\text{Al}_3$ for $x = 0.3, 0.5, 0.65$ and 1.0 . Over a wide temperature range as shown in Fig. 10⁹⁴. This has been shown to be the case for a number of amorphous alloys such as $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$,⁴¹ $\text{Fe}_{81}\text{B}_{13.5}\text{Si}_{3.5}\text{C}_2$ etc., studied by Mossbauer spectroscopy.⁴² Low temperature magnetisation studies also give identical results^{89,90}. On the same system there is fair agreement in the temperature range over which $T^{3/2}$ dependence is observed.^{88,94,95} A closer inspection of these data reveals several differentiating features between crystalline and amorphous alloys. For a ferromagnet, in the crystalline state, crystal momenta are quantised and the conventional spin wave theory leads to the following relationship between B and C in eqn. (2) and the spin-wave stiffness constant D :

$$B = \zeta\left(\frac{3}{2}\right) \left[\frac{g\mu_B}{M(O)} \right] \left(\frac{k_B}{4\pi D} \right)^{3/2} \quad (10)$$

and

$$C = \zeta\left(\frac{5}{2}\right) \left[\frac{g\mu_B}{M(O)} \right] \left(\frac{k_B}{4\pi D} \right)^{5/2} \left(\frac{3\pi \langle r^2 \rangle}{4} \right), \quad (11)$$

where $\zeta(3/2) = 2.612$ and $\zeta(5/2) = 1.341$ are the Reiman zeta functions and $\langle r^2 \rangle$ is the average mean square range of the exchange interaction and the other symbols have their usual significance. In crystalline systems it is found that $T^{3/2}$ dependence based on eqn (2) is restricted to $\sim 0.15T_c$. In striking contrast, in amorphous alloys $T^{3/2}$ dependence is found to be valid from $0.2T_c$ even upto $0.4T_c$. In $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$, for instance low temperature magnetisation measurements show $T^{3/2}$ dependence upto $\sim 0.35T_c$.⁸ Secondly, the values of $B_{3/2}$ are four to five times larger in amorphous alloys than values observed for crystalline systems and is definitely characteristic of the glassy state. They all exhibit comparable values for

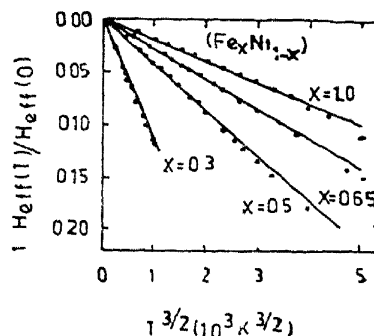


FIG 10 Plot of $1 - H_{\text{eff}}(T)/H_{\text{eff}}(O)$ vs $T^{3/2}$ in $(\text{Fe}_x\text{Ni}_{1-x})_{75}\text{P}_{16}\text{B}_6\text{Al}_3$ ⁹⁴

the coefficient of $T^{5/2}$ term. The values obtained for various systems are compared with crystalline systems in Table IV. Chien and Hasagawa⁹⁶ have explained the $T^{3/2}$ dependence over a wider temperature range on the basis of the relative values of B and C in eqn (9). For crystalline ferromagnets $C_{5/2}/B_{3/2} \simeq 1$ and for amorphous ferromagnets it is significantly less and is ~ 0.3 . It has been shown that such a result can be computer simulated for an amorphous ferromagnet with damped short-range interactions.⁹⁷ This implies that a description by localised spins with short-range interactions is closer to the real situation in amorphous ferromagnets. The large B also implies smaller D , the spin-wave stiffness constant. In general, that the stiffness constant D of amorphous ferromagnets is less than that of corresponding crystalline ferromagnets implies that spin waves in amorphous ferromagnets have lower energies of excitation. This is in agreement with the theoretical result of Tahier-Kheli's⁸⁵ random bond model where the density of states $\rho_{am}(W)$ is shown to have a form reproduced in Fig 11. The result also will mean that as temperature increases magnetisation falls more rapidly in amorphous systems than for the crystalline systems which are composition-wise comparable and the curie temperature is lower for the amorphous ferromagnet. These results are in broad agreement with experimental observations.²

TABLE IV

Comparison of critical constants for amorphous ferromagnets and crystalline systems^{94,99}

	$B(10^{-6}\text{K}^{-4/2})$	$C(10^{-8}\text{K}^{-3/5})$	$B_{3/2}$	$C_{5/2}$	$T_c(\text{K})$
$\text{Fe}_{75}\text{P}_{16}\text{B}_6\text{Al}_3$	18.6	—	—	—	630
$(\text{Fe}_{0.30}\text{Ni}_{0.70})_{75}\text{P}_{16}\text{B}_6\text{Al}_3$	124	—	—	—	258
$\text{Fe}_{10}\text{Ni}_{70}\text{B}_{19}\text{Si}_1$	212	23.2	0.54	0.110	186.5
$\text{Fe}_{13}\text{Ni}_{67}\text{B}_{19}\text{Si}_1$	127	9.7	0.56	0.115	268.5
$\text{Fe}_{20}\text{Ni}_{60}\text{P}_{14}\text{B}_6$	154	13.9	0.53	0.100	228
$\text{Fe}_{29}\text{Ni}_{49}\text{P}_{14}\text{B}_6\text{Si}_2$	70	3.7	0.51	0.100	375
Crystalline Fe	3.4	0.1	0.115	0.040	1043
Crystalline Ni	7.5	1.5	0.119	0.150	631

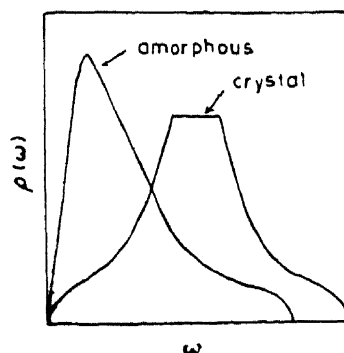


FIG 11 A schematic representation for the spin-wave density of states in an amorphous ferromagnet.

A scrutiny of the published low temperature neutron diffraction and magnetisation data in crystalline ferromagnetic metals shows a linear correlation between $T_c^{3/2}$ and $1/B$ ⁹⁸. Similar is found to be the case for amorphous ferromagnets as well with however the essential difference that the data lie well below those for crystalline ferromagnets. Such a linear correlation between $B_{3/2}$ and $T_c^{3/2}$ means that D is directly proportional to T_c . This is substantiated by the observations on $a\text{-Fe-B-X}$ ($X = \text{P, C, Si, Ge}$) and $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20-x}\text{P}_x$ alloys^{99,100}. It has been however pointed out that extrapolation of these data lead to zero D values for finite value of T_c , a result inconsistent with the prediction of a theory proposed by Katsuki and Wohlfarth¹⁰¹ based on the itinerant electron model. Such a discrepancy may be attributed to errors in extrapolation from large T_c values. Kaul,⁸⁹ on a similar investigation has shown that amorphous nickel-rich transition metal-metalloid alloys having a wide range of T_c values show a linear relationship between D and T_c . Such a plot is found to have a finite D value for $T_c = 0$ whereas for the nearest neighbour Heisenberg model for $S = 1$, the theoretical variation predicts $D = 0$ for $T_c = 0$ (Fig. 12). This has been explained by assuming a relationship of the form $D = D_0 + mT_c$. Similar result has been obtained for the amorphous alloys $(\text{Fe}_{1-x}\text{Ni}_x)_{77}\text{Si}_{10}\text{B}_{13}$ and $(\text{Co}_{1-x}\text{Ni}_x)_{75}\text{P}_{16}\text{B}_8\text{Al}_3$.^{102,103} This result *viz.*, the plot between D and T_c has a positive intercept for $T = 0$, has been explained in terms of direct exchange interaction involving not only the nearest neighbours but also the next nearest neighbours⁸⁹.

In principle, measurements leading to spin-wave stiffness constant D should be considered by considering both spin-wave and single particle excitations. It turns out that the latter contributions are not significant in a -alloys such as $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$, Fe-Ni-P-B alloy⁸⁸. This, however, is not always the case. The itinerant electron model, although is conceptually more difficult to apply, it is considered to be more appropriate as it encompasses many of the 'localised' features as well. Wohlfarth¹⁰¹ has attempted a judicious blend of theory and empiricism to enable experimentalists to apply the itinerant electron model to complicated alloys, such as the amorphous magnets. Within the Stoner-Wohlfarth model for homogeneous weak itinerant ferromagnets the following relations are obtained —¹⁰⁴

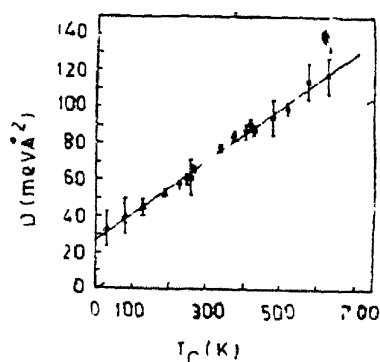


FIG 12 Spin-wave stiffness constant D vs Curie temperatures of various transition metal-metalloids⁸⁹

(i) The functional dependence of magnetisation on the field H and temperature T is given by

$$[\sigma(H, T)]^2 = [\sigma(0, 0)]^2 \left[1 - \left(\frac{T}{T_c} \right)^2 \right] + 2x(0, 0) \left[\frac{H}{\sigma} \left(\frac{H}{T} \right) \right] \quad (12)$$

where $x(0, 0)$ is the zero-field differential susceptibility at 0 K. This relationship implies that $[\sigma(H, T)]^2$ vs. $H/\sigma(H, T)$ isotherms in the temperature range $T \ll T_c$, where T_c is related to the density of single particle states at the Fermi level, should be a set of parallel lines. These plots are referred to as the Arrot Belov Kouvel (ABK) plots

(ii) The above mentioned isothermal plot should pass through the origin for $T = T_c$. The slope and intercept of such a plot gives $2x(0, 0) [\sigma(0, 0)]^2$ and $[\sigma(0, T)]^2$ which according to eq. (12) is equal to $[\sigma(0, 0)]^2 [1 - (T/T_c)^2]$, respectively. This result means that $\sigma^2(0, T)$ vs. T^2 plots should be linear. $\sigma(0, 0)^2 \sim T_c^2 \sim \chi(0, 0)^{-1} |C - C_{crit}|$ and $q_c/q_s \sim T_c^{-1}$, where q_c and q_s are the magnetic moments per atom deduced from the Curie Weiss constant and saturation magnetisation respectively. In the exceptional case of α -Y₂Ni_{1-x} the linear relationship between $\sigma(H, T)^2$ vs. T^2 has been observed both over a very wide range of temperature as well as concentration^{104,105}. The ABK plots which have been obtained for several amorphous alloys such as α -Ni₈₄P₁₆, α -Ni_{48.2}Cu_{51.8}, M_{90} Zr₁₀ ($M = \text{Fe, Co, Ni}$) do show linearity over a wide range of $H/\sigma(H, T)$ value.^{104,106} These plots show curvatures which change from converse to concave as T passes from values above T_c to below T_c and are almost symmetrical about T_c . The deviations from linearity at low fields has been attributed to concentration fluctuation of the magnetic atoms within the ferromagnetic phase¹⁰⁴

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METAL INSULATOR TRANSITIONS

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A metal may turn insulator due to increasing electron correlation (Mott) or disorder (Anderson) or electron lattice coupling, or a combination of these. The first two mechanisms are reviewed here briefly. Attempts to describe what happens when both are present, are also summarized. Finally some comments are made on criteria for the transition, effects of electronic (in) commensuration and disorder as well as on heavy fermions.

Key Words : Metal Insulator Transitions; Mott Electron Correlation; Anderson Disorder; Electron Lattice Coupling; Heavy Fermions; Coulomb Interactions; Orbital Effects; Doped Semiconductors; Electronic Incommensuration

INTRODUCTION

THE transformation of a substance from metal to insulator on varying a physical parameter such as temperature or pressure or disorder is often due to a basic change in electronic bonding. In the solid state, the change is best studied through physical properties and thus the subject is of interest both as chemistry and physics. In spite of extensive work in this field by chemists and physicists, and a general agreement on model patterns, we are far from a full understanding of the phenomena. In this brief review, I shall sketch some simple models, and will conclude with some comments. The subject has been extensively discussed many times, the book by Mott¹ is a comprehensive and unique survey of the experimental and theoretical situation as of a decade ago. A recently published Festschrift for Mott describes the present state of the subject.²

Some of the questions involved are most easily brought out by considering a model system, namely a periodic lattice of hydrogen atoms, first discussed by Mott.³ The lattice structure is assumed to remain uncharged, so that the single relevant variable is the lattice constant b . If b is small, electronic overlap is large, and the system is a metal according to one electron band theory, the highest occupied band being half full. The electronic states are best described as molecular orbitals. On the other hand, suppose b is very large (i.e. $b \gg a_0$ the Bohr radius), the system is then best viewed (to zeroth order) as a lattice of isolated hydrogen atoms, i.e. a Heitler London or atomic description is a good starting point. In this limit, electron motion is activated, the activation process being the removal of an electron from 'its' proton and attachment to a nearby neutral atom. The activation energy is $U = I - A$, I being the ionization energy and A the electron affinity. The system is thus an insulator. In the band picture, the system

always ought to be a half-filled band metal, albeit with a greatly reduced bandwidth as b increases. In fact, however, one expects to pass from a metal to an insulator, because the nature of electronic states changes from extended and uncorrelated (band like) to localized and correlated (atomic like). What is the nature of this transition? Does it occur at a critical value b_c of the lattice constant b ? Is it continuous or discontinuous? How do measured properties such as electrical conductivity, electron excitation spectrum and magnetic susceptibility vary across the transition? Is it accompanied by structural and magnetic changes?

One can sense, from the fact that the two phases are most simply described in very different chemical terms, that the theoretical problem is difficult. Experimentally, the above questions have been extensively investigated for a large number of substances; an important question is the relationship between these observations and predictions of the above simplified model. Another question, first discussed by Mott,⁴ is of experimentally studying hydrogenic systems so that the basic phenomenon of correlation driven metal insulator transition (Mott transition) can be most clearly exhibited. Mott pointed out that since shallow donor and acceptor states are large and hydrogenic, the insulator metal transition that occurs with increasing dopant concentration ought to be an attractive possibility.

However, even in the relatively simple model case of a hydrogen atom lattice, a number of complications are possible, and do occur. For example, the actual low density ground state is a lattice of hydrogen molecules. In the above description, this possibility, namely that of unit cell doubling by lattice deformation has been ignored. Since now the unit cell has two electrons, the system can be insulating even in one electron band theory. The metal insulator transition can thus be driven by electron ion or electron lattice interaction rather than electron correlation. The actual nature of the proposed model system, e.g., phosphorus-doped silicon, points to another factor, namely disorder. The physical parameter in Si:P is the phosphorus density n , the critical value for the insulator metal transition being $n_c = 3.8 \times 10^{18}/\text{cc}$. The system is hydrogenic and the electron lattice interaction effect is weak since the basic electronic scale is $a_0^* \approx 30\text{\AA}$, much larger than the lattice constant. However, since phosphorus atoms *randomly* substitute Si atoms, one does not have a periodic system. The quantum mechanical matrix elements for an electron to hop from one P atom to the next vary over a *very* wide range. It was first realized by Anderson⁵ that this kind of randomness by itself (i.e. even in the absence of correlation) can localize electronic states. The question of whether the observed metal insulator transition in P doped Si arises from correlation or disorder or from a combination, is still not settled, as we shall see.

In the succeeding section of this paper, we review the Mott transition (Section II) and the Anderson transition (Section III). The former is discussed mainly in a simple model due to Hubbard^{6,7} and a number of realistic features ignored in the model are mentioned. In Section IV, we outline the present theoretical understanding of metal insulator transitions with both disorder and interaction effects present. The properties of the experimentally well-studied Si:P system are then described (Section V). We conclude with comments on the possible

range of phenomena near the metal insulator transition, and point out how detailed experimental studies can point to the mechanism or mechanisms involved (Section VI)

II MOTT TRANSITION

Perhaps the simplest model for correlation effects in solids goes by the name of Hubbard^{6,7} One imagines an orbitally non-degenerate atomic state at each lattice site i , thus there can be zero, one or two electrons (one with spin up and the other with spin down) at the site i . The energies are 0, $\epsilon_{i\sigma}$ and $(\epsilon_{i\uparrow} + \epsilon_{i\downarrow} + U)$ respectively. The extra energy cost U of a two electron configuration is the sole measure of correlation. It is effective only on site. An electron hops from site i to site j with an amplitude t_{ij} . Usually t_{ij} is taken to be nonvanishing only between nearest neighbours, z in number, and to have the same value of t for all of them. The model is then characterized by single dimensionless ratio (zt/U) and by a (kinetic) energy scale zt . As (zt/U) decreases, one goes over continuously from a molecular orbital to a Heitler London limit. The Hamiltonian is

$$H = \sum_{i,\sigma} \epsilon_{i\sigma} n_{i\sigma} + \sum_{i,j,\sigma} t_{ij} a_{i\sigma}^\dagger a_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} \quad \dots(1)$$

The electron density or the average number n_e of electrons per site is another important parameter.

The system described by the above model Hamiltonian clearly has a metal insulator transition for exactly $n_e = 1$ (one electron per site) when U is sufficiently large. In general, a system can be insulating for any commensurate filling, i.e. integer number of electrons per site, if correlation effects are strong. In the insulating phase, since the spin of the electron is localized as well, the solid has magnetic moments. They interact antiferromagnetically, with the nearest neighbour coupling energy (t_{ij}^2/U) so that the ground state is antiferromagnetically ordered. It is an interesting but scarcely explored prediction that for $n_e \neq 1$, the system is a metal no matter how strongly correlated it is. The reason is that the extra electrons or holes (for $n_e > 1$ or $n_e < 1$ respectively) are always mobile, there being more equivalent sites than carriers.

The possible phases of the Hubbard model have been investigated mainly in the one body or Hartree-Fock approximation⁸. The correlation term $U n_{i\uparrow} n_{i\downarrow}$ which depends on the actual number of up and down spin electrons at site i is approximated by the spin potential due to the *average* number of electrons of the other spin, i.e. one writes

$$U n_{i\uparrow} n_{i\downarrow} = U n_{i\uparrow} \langle n_{i\downarrow} \rangle + U n_{i\downarrow} \langle n_{i\uparrow} \rangle - U \langle n_{i\uparrow} \rangle \langle n_{i\downarrow} \rangle \quad (2)$$

Now since the number of electrons per site $\langle n_{i\uparrow} \rangle + \langle n_{i\downarrow} \rangle = n_e$ is fixed, there is one unknown parameter, i.e., the magnetization $m_i = \langle n_{i\uparrow} \rangle - \langle n_{i\downarrow} \rangle$ per site. This parameter is determined in the usual way, i.e. the ground state of the approximate Hamiltonian of eqs (1) and (2) is found, the quantities $\{m_i\}$ calculated from this, and the process iterated to self-consistency. It is not possible to do this

ctivity calculation. A region of first order transitions (shown by full lines) may also be an artefact of the approximations used.

The one body approximation is a symmetry breaking mean field theory. It breaks the symmetry between up and down spins even in the paramagnetic state, e.g. M' and I , where moments are present but not ordered. The mean field is the local magnetization. The approximation is a good first order theory if the mean field is large ($m \simeq 1$) and transitions between the two broken symmetry solutions at each site (i.e. $\pm m$) i.e. spin fluctuations occur only on a long time scale. Deep inside the insulating regime, it is indeed true that m is close to unity, spin fluctuations are slow (rate $\Gamma \simeq zt^2/U$), and that charge or valence fluctuations are strongly suppressed because of strong correlation effects. However, in the metal insulator transition regime, charge fluctuations, spin fluctuations, temperature and mean field all have a comparable energy scale, so that the Hartree Fock approximation is specially bad.

A different kind of approach which emphasizes local correlation effects is due to Gutzwiller.⁹ Brinkman and Rice¹⁰ pointed out its relevance for the metal insulator transition due to correlation. The idea is to write down an approximate ground state wave function incorporating correlation effects, these discourage double occupancy of any site. The wave function is

$$\psi_G = \prod_i [1 - (1 - g) n_{i\uparrow} n_{i\downarrow}] \psi_F \quad (3)$$

Here ψ_F is the uncorrelated or free Fermi or MO ground state which is exact for $g = 1$. For $g = 0$, it is clear that the ground state has no doubly occupied sites. The parameter g is thus a measure of correlation and is determined variationally. An approximate calculation shows that $g \rightarrow 0$ as $U \rightarrow U_c = -8 \sum_{k(\text{occ})} t_k$. As the

Hubbard correlation increases towards U_c , electrons get locked to their 'respective' sites, i.e. there is both spin and charge localization. This is reflected in both the spin susceptibility and effective mass diverging as $(U_c - U)^{-1}$. One thus has a strongly correlated heavy Fermi system on the verge of transition to a correlation localized or Mott insulating phase. The approximation thus provides an attractive picture of the situation near the transition. However, the insulating phase, and ordering therein are not described, nor are the $T \neq 0$ properties. Spatial correlations are completely ignored.

Metal insulator transitions in transition metal oxides, with V_2O_3 being the most extensively studied example, do have features of the sort discussed above. The phase diagram of V_2O_3 doped with Cr and Ti (supposed to uniformly dilate or contract the lattice) is shown in Fig. 2. There is a metallic phase, an antiferromagnetic insulating phase and disordered insulating phase. The transitions are all first order except that the $M-I$ transition ends in a critical point. The broad similarity between Figs 1 and 2 is apparent. The observed transitions are probably first order because of electron lattice coupling. However, the magnetic susceptibility, electronic heat capacity, and T^2 coefficient of resistivity are all enhanced by a factor to 20 to 50 with respect to typical transition metal values. This is suggestive of

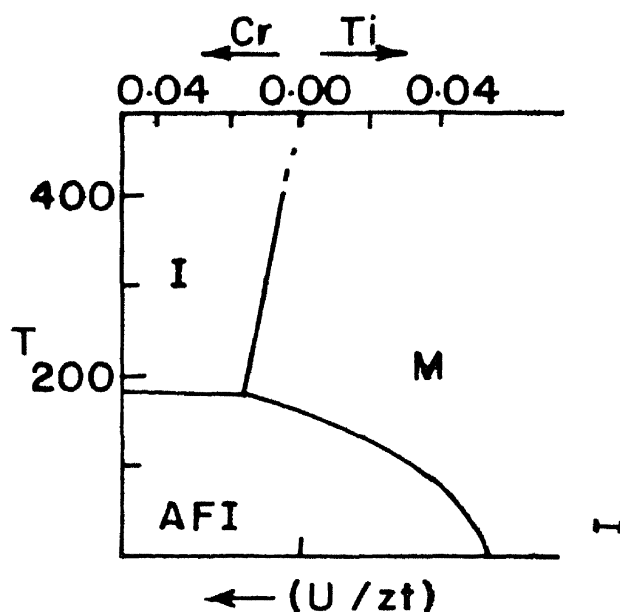


FIG 2 Phase diagram for V_2O_5 alloyed with Cr and Ti. Metallic, insulating and antiferromagnetic insulating phases are shown. Full and broken lines indicate first order and continuous transitions respectively.

Brinkman-Rice type of critical correlation effects preceding a metal insulator transition. The fact that the resistivity of the metal near the metal insulator transition is very high implies also that strong disorder effects are present.

The main conclusion is that even for this simple model, the nature of the metal insulator transition is not understood in detail.

Shortcoming of the Model

The Hubbard model does not describe realistically any known physical system. Some of the features which could be relevant and have been left out are the following:

Orbital Effects Metal insulator transitions occur most commonly in systems based on transition metal atoms which have large orbital degeneracies N . Atomic and solid state features such as Hund's rule coupling, configurational splitting, spin-orbit coupling, crystal field lifting of orbital degeneracy, are all neglected. These degrees of freedom may have qualitative effects, e.g. orbital superlattice formation.¹¹ An important quantitative consequence could be that intersite energies are disfavoured by a $(1/N)$ factor relative to intra or single site energies.^{12,13}

Another recently discussed effect is due to the presence of other bands, e.g. states of s or p local symmetry. An example is NiO , an insulator due to correlation effects. The lowest excitation gap (e.g. the conductivity gap) is not $U_{dd} \approx 10\text{eV}$, but is about 2eV , this being the energy required to remove an electron from the filled oxygen p band and to put it into a $Ni\ d$ -orbital. Such a system is most naturally described as a charge transfer insulator. A one site theory of energy level spectra

of such systems has been discussed recently by Sawatzky and Allen,¹⁴ comparison being made with photoemission experiments. Hufner¹⁵ has recently suggested, on the basis of such data and charge transfer spectral energies, that in the 3d series, the first half atoms (e.g. Ti, V) are likely to form Mott insulators with U_{dd} as the relevant electronic gap (Mott insulators) while those in the second half (e.g. Fe, Ni) are likely to form charge transfer insulators. It should be noted however that electron correlation is the basic cause of the insulating phases in either case. The second class of systems are best described as Anderson lattices, i.e. as lattice generalizations of a model for a magnetic impurity in a metal involving correlated d or f states, conduction band s or p states, and hybridization or admixture.

Coulomb Interaction In the Hubbard model, electrons interact only when on the same site. In fact, the coulomb interaction is unscreened and of long range for the insulator. Mott³ pointed out that consequently the 'electron' 'hole' excitations (with respect to the lower Hubbard band filled ground state) attract and form bound states. The system thus continues to be insulating unless the number of electrons and holes is large enough so that the screened interaction is too weak to bind. At this point there is a discontinuous jump in the carrier density, so that the insulator metal transition is first order. Thus the coulomb interaction because of its long range can change the character of the transition. The argument relies on the 'electrons' and 'holes' being well defined (long lived) excitations. For $U \simeq U_c(zt)$ the Hubbard gap is small, and this assumption may be incorrect. The question is not settled, especially since the hydrogenic system Si-P has a *continuous* metal insulator transition.

Electron Lattice Interaction. The electronic energy depends strongly on ionic positions for d electron as well oxygen and chalcogen states. Especially when the electronic state tends to localize, this electron lattice interaction is effectively stronger, and almost inevitably causes lattice distortions. The interplay between correlation and electron lattice distortion has not been explored seriously except for one dimensional systems. We briefly mention here two ideas developed for the situation where electron lattice interaction only is present. It is generally believed¹⁶ that when electron acoustic phonon (lattice distortion) coupling λ exceeds a certain strength the local distortion produced by the electron traps it (small polaron). Thus with increasing λ , there is a very rapid increase of electron effective mass around a particular value λ_c . This is obviously relevant to metal insulator transitions in two ways. Such as a very narrow band system can become insulating with even a modest correlation U . Secondly, correlation can help in selftrapping. The other idea concerns the possibility of a bipolaron formation. Two close polarons may be more stable due to the extra lattice distortion caused lowering of energy than two polarons far away which repel each other because of the coulomb interaction.¹⁷ Interestingly, there also seems to be a regime where a small bipolaron is stable whereas two small polarons are not. In a lattice, such a bipolaron formation could be the driving force for a characteristic metal insulator transition to a molecular crystal like phase which is a diamagnetic dimerized solid. The transition is most likely discontinuous.

Disorder The high electrical resistivities of the metallic phase near the transition and their anomalous dependence on temperature imply the existence of strong disorder. The theory of strongly correlated and disordered systems is not well developed, but there has recently been considerable progress in the theory of disordered electronic systems close to localization (Anderson localization)¹⁸. We now discuss this route to the metal insulator transition.

III ANDERSON LOCALIZATION

Consider for concreteness a model similar to that used above, i.e. eq (1). However, one assumes that there is no correlation between electrons, but that the energies ϵ_i at the sites i are random. The randomness can be characterized by a spread of width W . Anderson⁵ showed that when this exceeds a critical value, an electron locates itself around an appropriate potential fluctuation so that the state is spatially localized rather than extended as it is for weak disorder. The critical value W_c , i.e. the ratio (W/zt) depends on the energy of the electron, and the dimensionality as well as the connectivity of the lattice. The consequences of this localization were first spelt out by Mott^{19,20}. Since the localization criterion depends on electronic energy, some states are extended and others localized for a given disorder. The sharp energy separating these is the mobility edge. A system is metallic or insulating depending on whether states near the Fermi energy are extended or localized. Now, with increasing disorder or decreasing Fermi energy or a combination of the two, the mobility edge energy crosses the Fermi energy and the system goes insulating. This type of metal insulator transition (Anderson transition) has been observed in a large number of systems, e.g., atomically disordered metal semiconductor composites ($\text{Nb}_x\text{Si}_{1-x}$, $\text{Au}_x\text{Ge}_{1-x}$), granular metal systems, metal inert gas mixtures. Our present understanding of the transition is summarized below.

If the single particle energy ϵ_i is the same at every site i , one has an electronically periodic solid, and the eigenstates are Bloch waves. For weak disorder (i.e. $W \ll zt$), the Bloch waves are scattered occasionally. The residual or $T = 0$ conductivity σ is given in terms of the mean free path l by

$$\sigma = \left(\frac{ne^2}{\hbar k_F^2} \right) (k_F l), \quad (3)$$

where n is the electron density and k_F is the Fermi wavevector. As disorder increases, the mean free path decreases. This mode of description fails when mean free path becomes of the order of or smaller than the interatomic spacing, i.e. for $k_F l \sim 1$. This is the minimum possible conductivity of a metal, a concept due to Mott²⁰. The minimum metallic conductivity of a metal in three dimensions is $\sigma_{\min}^{3d} = (e^2/3\hbar\pi^2) k_F$ and in two dimensions it is $\sigma_{\min}^{2d} = (e^2/2\hbar\pi^2)$. We note that these values, involving quantum diffusion depend on Planck's constant $\hbar$, and that in two dimensions $\sigma_{\min}$ depends only on fundamental constants. The conductivity of a metal drops abruptly from $\sigma_{\min}$ to zero at the metal insulator transition. There

is a very large amount of experimental evidence for a change of transport regime in disordered systems near $\sigma_{\min}$. For example, the temperature coefficient of resistivity changes sign when $\sigma \sim \sigma_{\min}$. In many cases the boundary between metal and insulator does seem to be at $\sigma_{\min}$ ²⁰ However, careful recent experiments at low temperature very close to critical disorder strongly suggest that zero temperature conductivity actually goes continuously to zero at the localization transition (see below).

On the localized side of the transition, as the metallic phase is approached, the localization length ξ increases and diverges, e.g. $\xi \sim (W - W_c)^{-1}$ where W_c is the critical disorder. The polarizability goes as ξ^2 , and ignoring local field corrections in this random system, the static dielectric constant ϵ also diverges as ξ^2 or $(W - W_c)^{-2}$. In this picture, the localization transition is asymmetric, discontinuous from the metallic side, and being continuous from the insulating side. The asymmetry is due to neglect of interference effects in the former regime. Localization is due to destructive interference of waves scattered repeatedly back and forth in the random medium. Just above critical disorder, the interference effect localizes electronic states over a diverging length scale ξ . However, just below critical disorder it is assumed that this interference has no effect on physical properties so that the conductivity σ has the same value at all length scales larger than the mean free path l .

In the scaling theory of localization²¹ account is taken of scale dependent interference effects. The localizing process is singular backscattering. The amplitude for an electron to go from one point to another is a weighted sum over the partial amplitudes for various paths. On these, consider the ones with a loop. This loop can be transversed in opposite senses (in the random medium) and the partial amplitudes are the same. Thus the probability (amplitude²) for return to the origin of the loop is enhanced because of backscattering interference. Neighbouring paths mute this effect, but it is still crucial in three dimensions. Based on this idea, the zero temperature conductivity near W_c is seen to be

$$\sigma(T=0) (e^2/\hbar\pi^2) \left(\frac{1}{\xi_{>}} \right) = \left(\frac{e^2}{\hbar\pi^2 l} \right) \left(\frac{W_c - W}{W} \right) \quad (4)$$

The first term in the last equation is the Mott $\sigma_{\min}$ and the second term is the reduction due to quantum interference. The conductivity thus goes to zero smoothly, being characterized by a length $\xi_{>}$ which diverges the same way as the localization length ξ on the other side. This is just like any continuous phase transition with a single diverging correlation length. A detailed analogy with a phase transition is possible using a field theory mapping of the problem due to Wegner²². The diffusion constant is analogous to the spin wave stiffness of a ferromagnet. In the localized regime, the effective spin wave stiffness at long length scales is zero.

In addition to the above, a number of detailed predictions for transport properties, e.g. temperature-dependence of resistivity and for magnetoresistance are possible. They are all based on the idea that backscattering interference is cut

off by temperature (inelastic scattering leads to incoherence) and by a magnetic field (which introduces a phase difference between the two oppositely traversed loop paths). The former implies that quantum interference effects decrease with increasing temperature. This means that resistivity can decrease with increasing temperature even in the metallic regime (i.e. one with $\sigma(T=0) \neq 0$). Also, a $\sigma_{\min}$ like behaviour can be inferred from higher temperature observations. The magnetoresistance is negative and has a characteristic $\sqrt{H}$ dependence in high fields.

A number of experiments have confirmed these predictions in great detail (including those for two dimensional systems)¹⁸. It is generally believed, since in a number of cases $\sigma < \sigma_{\min}$ has been observed with the dependence of eq. (4), that the localization transition is continuous (see however the detailed analysis of Mobius for a contrary view²³). We now turn to a discussion of what is expected when disorder and interaction are both present.

IV DISORDERED INTERACTING SYSTEMS

Most theories of such systems are perturbative, i.e. they describe the weakly disordered, weakly interacting metal, and seek to extrapolate from this limit. Perhaps the only exception is the theory of Efros and Shklovskii¹⁸ for the coulomb interaction effects in the highly localized regime (i.e. extremely strong disorder). Altshuler and Aronov^{24,25} were the first to realize that in a disordered system interaction effects are characteristically different. The extension of these to the metal insulator transition regime, using scaling ideas, is due to McMillan²⁶ and a number of others¹⁸. There are no theories yet which treat interaction or correlation effects exactly or accurately enough to lead to the Mott transition, *and* include disorder effects.

In a disordered medium, electrons move diffusively, i.e. separation increases as the square root of time rather than as time. This effectively enhances the interaction and makes it retarded. For example, the probability for an electron to be at r at a time t starting from $r=0$ (at $t=0$) is $P(r, t) \sim (1/Dt)^{3/2} \exp(-r^2/Dt)$. Thus the probability that two initially close electrons stay close ($r \sim 0$) is proportional to $(1/Dt)^{3/2}$. Two such electrons with energy difference E stay coherent for a time $t \sim (h/E)$, so that the probability that they stay near each other and interfere is

$$P(E) \simeq \int_0^{(h/E)} P(t) dt \simeq E^{1/2}/D^{3/2} \quad (5)$$

This leads to several characteristic and novel effects, some of which are listed below —

(i) There is square root cusp $\delta N(E)$ in the density of states $N(E)$ as a function of energy E (with respect to the Fermi energy). The cusp is generally a dip, and is given by

$$\frac{\delta N(E)}{N(0)} = \frac{V(0)}{4\pi^2(dn/d\mu)} \frac{N(0)}{D} \left(\frac{E}{D}\right)^{1/2},$$

where $V(0)$ is the zero range interaction strength, and $(dn/d\mu)$, is the compressibility. The effect obviously becomes stronger with increasing disorder (decreasing D)

- (ii) There is a $\sqrt{T}$ term in resistivity, the sign depending on details of interaction strengths in various partial wave channels. It is generally negative
- (iii) There can be a positive magnetoresistance due to spin splitting, with a $\sqrt{H}$ field dependence for $\mu H > k_B T$
- (iv) There is a temperature-dependent spin susceptibility enhancement.
- (v) Inelastic decay rates, e.g. due to electron-electron interaction are enhanced. For example in three dimensions, the rate is $\Gamma(E, T) \sim \{\max(E, T)\}^{3/2}$ in contrast to the quadratic dependence for pure system. Consequently, inelastic mean free paths are much shorter in disordered systems than in clean systems

Many of these effects have been quantitatively confirmed in metallic glasses, disordered metals, doped semiconductors etc

Interaction effects clearly become more pronounced as disorder increases. Also, as the density of states depletion becomes larger, screening becomes poorer, and the interaction strength increases. Thus there is a nonlinear feedback effect leading to an interaction and disorder dominated metal-insulator transition. A schematic scaling model for such a transition was first presented by McMillan²⁶ and more carefully and extensively by Finkel'shtein²⁷ and Castellani *et al*²⁸. A number of scenarios have been worked out, we summarise two below —

One is interested in the effective interaction between electrons at long length and time scales, given their values at short scales l (mean free path) and τ (collision time) respectively. This effective coupling is influenced by diffusive electronic motion and by interaction between various modes (density fluctuations, spin fluctuations, electron pairs). It is obtained by progressively integrating out effects on length and time scales longer than l and τ respectively. The modes can be characterized by total spin, which is conserved. The spin singlet ($S = 0$) electron-hole mode corresponds to an orbitally symmetric, mainly isotropic (s -wave) scattering and describes pure density fluctuations in the latter case. Similarly, the $S = 1$ or spin triplet mode with p -wave orbital character, describes spin fluctuations. We ignore higher l partial wave interaction. In the particle-particle channel, only the $L = 0, S = 0$ or Cooper channel is considered significant. The model is thus characterized by three parameters corresponding to bare interaction strength in these channels, and by a diffusion constant D . The scaling theory with these four scale-dependent parameters has not yet been solved. We mention two special cases, considered to leading order in D^{-1}

(i) *Singlet Only*: This can be experimentally realized if there is considerable scattering by magnetic impurities. Such scattering leads to non-zero energy for long wavelength spin fluctuation and Cooper modes. One then has a system of *only* density fluctuations coupled by the Coulomb interaction. Altshuler and Aronov²⁵ show that the metal-insulator transition is continuous with $\sigma \rightarrow 0$ according

to the exponent unity. The dielectric constant diverges with the exponent $(3/2)$, the density of states at the Fermi energy varies as $\exp \{-1/8 (\ln T)^2\}$ and the ac conductivity as $\omega^{2/5}$. The conductivity exponent is the same as for pure localization, though the other exponents are different.

(11) *Singlet and Triplet* Suppose particle scattering is neglected. The effective spin-spin coupling becomes very large on scaling, and indeed diverges at a finite length scale l_c . At this length scale, density diffusion is non-zero, but spin diffusion vanishes. The spin susceptibility also diverges. One thus has a metal with clump of frozen magnetization on a length scale l_c , i.e. a local moment. Unfortunately, the perturbative scaling approach breaks down when coupling constants become large, and the above result for a $T = 0$ spin localization transition preceding a metal-insulator transition is only suggestive.

V. METAL INSULATOR TRANSITION IN DOPED SEMICONDUCTORS

We discuss this specific case because it has been studied experimentally in great detail, and because the system is relatively simple. As mentioned earlier, the uncompensated shallow donor/acceptor system is close to Mott's model for a lattice of hydrogen atoms except for considerable variation in intersite hopping energy. The earliest prediction was that because of electron hole attraction the transition would be first order, marked by a discontinuity in the carrier concentration. The observed transition is continuous. If the short range correlation or Hubbard U is the dominant interaction, then the transition (Hubbard-Mott) is continuous, from a localized spin insulator to a paramagnetic metal. With increasing compensation, correlation effects are reduced, and if randomness predominates, one expects an Anderson or localization transition. Mott suggested that this might continue to be true even for uncompensated systems. We thus have a variety of predictions depending on the dominant mechanism.

Experimentally, the conductivity of Si-P goes continuously to zero at the $T = 0$ metal-insulator transition, which occurs for $n_P \approx 3.8 \times 10^{18}/\text{cc}$. The exponent is half for uncompensated systems²⁹ and seems to be unity for compensated ones^{30,32} as also for a number of other systems³³. The conductivity exponent is unity in localization theory as also in one version of disordered electron gas theory (density fluctuations only, see above). An exponent of half is possible for a noninteracting disordered electron gas if singular backscattering effects are suppressed by magnetic impurities or a magnetic field. The static dielectric constant of insulating Si-P diverges with an exponent of unity³⁴. No theory yet predicts this exponent but the ratio of this and the conductivity exponent is two, the value expected in localization only theory, if only one scale parameter is relevant.

There is an increasing body of evidence pointing to strong spin correlation near the metal-insulator transition in doped semiconductors. First, far away from the transition, characteristic resistivity and magnetoresistance anomalies have the right size, and sign. Secondly, spin-lattice relaxation rates in the metal near the

metal insulator transition are singularly enhanced going as $T^{1/2}$ rather than as T for a Fermi system. This implies critical slowing down of spin diffusion, i.e. spin localization. Very recently, careful low temperature spin susceptibility measurements³⁶ show a large rise at temperatures below about 50mK. A similar but more modest specific heat increases in metallic systems farther from the transition has been observed earlier³⁷. All these observations remain basically unexplained, though an obvious suggestion is that a Brinkman Rice kind of enhancement, characteristically modified by disorder, is present near the transition.

The ac conductivity just on the insulating side has been measured recently³⁴. It is linear in frequency, and the coefficient diverges as the dielectric constant ϵ . Bhatt and Ramakrishnan³⁸ argue that this is direct evidence for Efros Shklovskii type of long range coulomb effects. In their absence, the coefficient would diverge as $\epsilon^{5/2}$ rather than ϵ , and the linear term would be proportional to $k_B T$. From the temperature-dependence of conductivity just on the insulating side, in *compensated* Ge : Sb, Zabrodskii and Zinoveva³¹ find similar effects, with a coulomb gap vanishing as one approaches the metallic phase.

It thus seems that disorder, short range Hubbard correlation, long range Coulomb interaction, and compensation are *all* important near the transition in doped semiconductors. There is a large discrepancy yet between these experimental observations and available theoretical models. This discrepancy is a measure of our current understanding of metal insulator transitions.

VI SOME COMMENTS

(i) Criteria for the Metal Insulator Transition

We consider here the question of whether agreement with a particular criterion is support for the related mechanism of metal insulator transition. The electron hole unbinding criterion of Mott implies that an insulator turns metallic when the carrier density n satisfies the equation

$$n^{1/3} a_H^* \simeq 0.25, \quad (6)$$

where a_H^* is a characteristic atomic spacing, i.e. shallow state radius, interatomic spacing, or atomic orbital size. To begin with, we note that the Mott criterion is spectacularly successful, over a density range of nearly 10^8 in doped semiconductors etc. even though the transition is continuous, and *not* first order as predicted by the mechanism underlying eq. (6).

Several different mechanisms lead to criteria similar to eqn. (6). For example, the Hubbard-Mott transition takes place when $zt \simeq U$. It can be shown for hydrogenic systems that this, as well as the Anderson localization criterion $\xi t \simeq W$ (the randomness of the one electron potential) amount to criterion similar to eqn. (6). Another criterion, due to Herzfeld, views the insulator as a lattice of nonoverlapping polarizable atoms of polarizability α , and considering local field corrections,

predicts for the dielectric constant $\epsilon_0 \left/ \left(1 - \frac{4\pi n}{3} \alpha \right) \right.$ where n is the atom density, clearly the dielectric constant blows up for $(4\pi n \alpha/3) = 1$ which *also* translates into a Mott like criterion. It is not clear whether this local field form survives when the electrons from neighbouring atoms overlap, and there is spatial randomness.

The reason different physical mechanisms lead to similar criteria is basically the following. The transition is due to a competition between potential and kinetic energies. The former localizes, the latter delocalizes. They depend differently on electron density, viz. as $n^{+1/3}$ and $n^{2/3}$ respectively, so that they are comparable when n satisfies the Mott criterion eq (6). Thus the criterion is inevitable on physical and dimensional grounds, and does not support any particular mechanism.

(ii) *Electronic Incommensuration*

In the Hubbard model, only the commensurate electronic system has a metal insulator transition; the incommensurate system is always metallic. However, if the system is random in addition, the Anderson localized insulating phase is a possibility. These and related questions have scarcely been explored seriously. For example, the metal insulator transition in V_2O_3 is affected much more by nonisoelectronic impurities than by isoelectronic impurities. The former favours the metallic phase strongly. In $LaNiO_3$ which could be described as a commensurate system with $U \simeq U_c$ (Brinkman-Rice correlated electron system) addition of a small amount of Cr or Mn (~ 2 per cent) Anderson localizes these almost spin localized states and leads to an insulating state.³⁰ A spectacular example of incommensuration effects is the drastic influence of oxygen vacancies on the Verwey transition in single crystal magnetite Fe_3O_4 .

A careful experimental study of this class of phenomena requires single crystals, electrochemical fine tuning of commensuration, and a wide range of experiments on transport and equilibrium properties. There are at present no theoretical results on highly correlated, disordered, incommensurately filled systems.

Incommensuration without disorder (especially weak incommensuration δ) in strongly correlated systems leads to characteristic behaviour associated with heavy fermions, e.g. low Fermi energy $\epsilon_F \sim \delta(zf)$, and presumably p wave superconductivity due to an electronic attraction mechanism. Such effects have so far been seen in actinide systems, e.g. UBe_{13} , UPt_3 .⁴¹ Here the f -shell is nearly integral valent, hybridization with s - p band leading to the small deficit. An obviously interesting questing question is whether transition metal based systems with similar properties exist. The proximity of a metal insulator transition, magnetic ordering, and superconductivity for large U , small incommensurations and weak disorder makes this regime very interesting.

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METAL-INSULATOR TRANSITIONS IN THE V_2O_5 ALLOY SYSTEM : EXPERIMENT AND THEORY

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A review is provided of a recent theory pertaining to properties of correlated electron systems, with particular application to the V_2O_5 alloy system. Correlation effects are introduced by specification of a parameter U/W , the ratio of intrasite Coulomb energies to bare-particle bandwidths. Under suitable conditions, a metal-insulator transition and its inverse may be brought about by increasing the temperature at fixed U/W . The conditions for bringing about reentrant metallic behaviour are specified in an appropriate phase diagram. The theory is then expanded to take into account transitions that occur at low temperature as a concomitant to the onset of antiferromagnetic order. Numerical results based on the above theory are compared with experimental work reported for the $(V_{1-x}Cr_x)_2O_5$ system; the results are in semi-quantitative agreement. It is pointed out that lattice effects must be included for a better description of the various metal-insulator transitions observed in this system.

Key Words : Electron, V_2O_5 Alloy and $(V_{1-x}Cr_x)_2O_5$ Systems; Correlation Effects; Coulomb Energy; Bare-Particle Bandwidths; Metal-Insulator Transitions

I. HISTORICAL INTRODUCTION

THE V_2O_5 system and its alloys with several transition metal oxides has been the subject of approximately 500 investigations ever since the report by Foex¹ of a phase transformation in V_2O_5 at 173 K. His dilatometric and resistivity measurements on compacted powder specimens were later confirmed by Morin² who reported on the electrical conductivity of V_2O_5 single crystals. Feinleib and Paul³ extended these measurements to higher temperatures where they encountered an additional resistivity anomaly in the range 350–650 K (see Fig 1c). MacMillan⁴ in an unpublished report first showed that a more complex set of transitions is exhibited by the $(V_{1-x}Cr_x)_2O_5$ alloy system in the range $0 < x < 0.1$. These studies were then continued by workers at Bell Laboratories^{5–7} who reported on the occurrence, with rising temperature, of an insulator-metal transformation in the range $25 < T_1 < 180$ K, and of a second metal-insulator transition in the range $180 < T_2 < 350$ K, the T_1 and T_2 values vary with x . The Bell group^{8,9} also studied the effects of incorporating Al_2O_3 , Ti_2O_3 , Fe_2O_3 , and other transition metal oxides into V_2O_5 , they

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and others^{10,11} further initiated a study of the changes in physical properties as the oxygen/metal ratio is altered. The Purdue research group^(12a,12b,13,14) enlarged on the earlier findings by reporting still another insulator-metal transition in the $(V_{1-x}Cr_x)_2O_3$ alloy system for $x > 0.005$ over a wide temperature range T_3 above 350 K, thus showing that such alloys exhibit reentrant metallic behavior. These later investigators also directed attention to sizeable hysteresis effects at T_1 and T_2 , and systematized the effects of incorporating Cr, Al, or Ti cations and cation vacancies. An enormous number of additional publications in the period 1945–85 has dealt with many other types of physical measurements on the above systems; for a dated review see Honig and Van Zandt.¹²

The current status of the field is perhaps best summarized in terms of Figs. 1(a)–(e) in which the resistivity ρ is plotted logarithmically against inverse temperature, T^{-1} . These schematic diagrams show a number of interesting features. For the V_2O_3 (98.5 per cent)– Cr_2O_3 (1.5 per cent) system one encounters the three transitions sketched out in Fig. 1(a). In the range between 0 and ~ 150 K the alloy is an antiferromagnetic insulator (AFI). There occurs a sharp transformation to the paramagnetic metallic state (PM) which prevails between ~ 150 and ~ 300 K. At that point another first order transition carries the system to a paramagnetic insulating state (PI). In the range ~ 300 –1000 K the resistivity gradually diminishes with rising temperature, so that beyond ~ 650 K the alloy system is in a high temperature paramagnetic metallic phase (PM') which closely resembles the PM configuration. This three-transition pattern may be readily altered by slight changes in alloying. The electrical properties of the V_2O_3 (97 per cent)– Cr_2O_3 (3 per cent) alloy system are sketched out in Fig. 1(b). It is seen that the PM phase is eliminated altogether, on heating, the alloy proceeds directly from the AFI to the PI configurations via a sharp ($x = 0.02 - 0.03$) or rounded ($x > 0.03$) transition, this is followed by a gradual changeover to the PM' state. In pure V_2O_3 the electrical resistivity exhibits yet a different pattern: as shown in Fig. 1(c), there is a large, first-order transition near 150 K which links the AFI and PM phases. With rising temperatures in the range 350–650 K an anomalous rise in resistivity takes place, so that undoped or lightly Cr_2O_3 -doped V_2O_3 passes continuously from the PM to the PM' configuration. Fig. 1(d) sketches the situation for V_2O_3 (99 per cent)– Ti_2O_3 (1 per cent) and for nonstoichiometric V_2O_3 . Basically, the AFI–PM transition is shifted to lower temperature and the resistivity discontinuity diminishes or increases with increasing Ti or cation vacancy content. Finally, as sketched in Fig. 1(e), when the Ti content is increased beyond 5.5 at per cent or the vacancy concentration passes beyond 0.9 at per cent all transitions are eliminated and only the PM phase is retained. However, below approximately 10–15 K the metallic phase transforms to an antiferromagnetic metal (AFM).^{13a} A phase diagram which summarizes the stability domains of the various phases is exhibited in Fig. 2, and the actual electrical resistivity measurements on which this diagram is based are displayed in Fig. 3(a), (b), and (c). The experimental work and the various features of the data have been explained elsewhere^{14,15} in great detail, this commentary will not be repeated here. Instead, we concentrate on the theoretical analysis of the

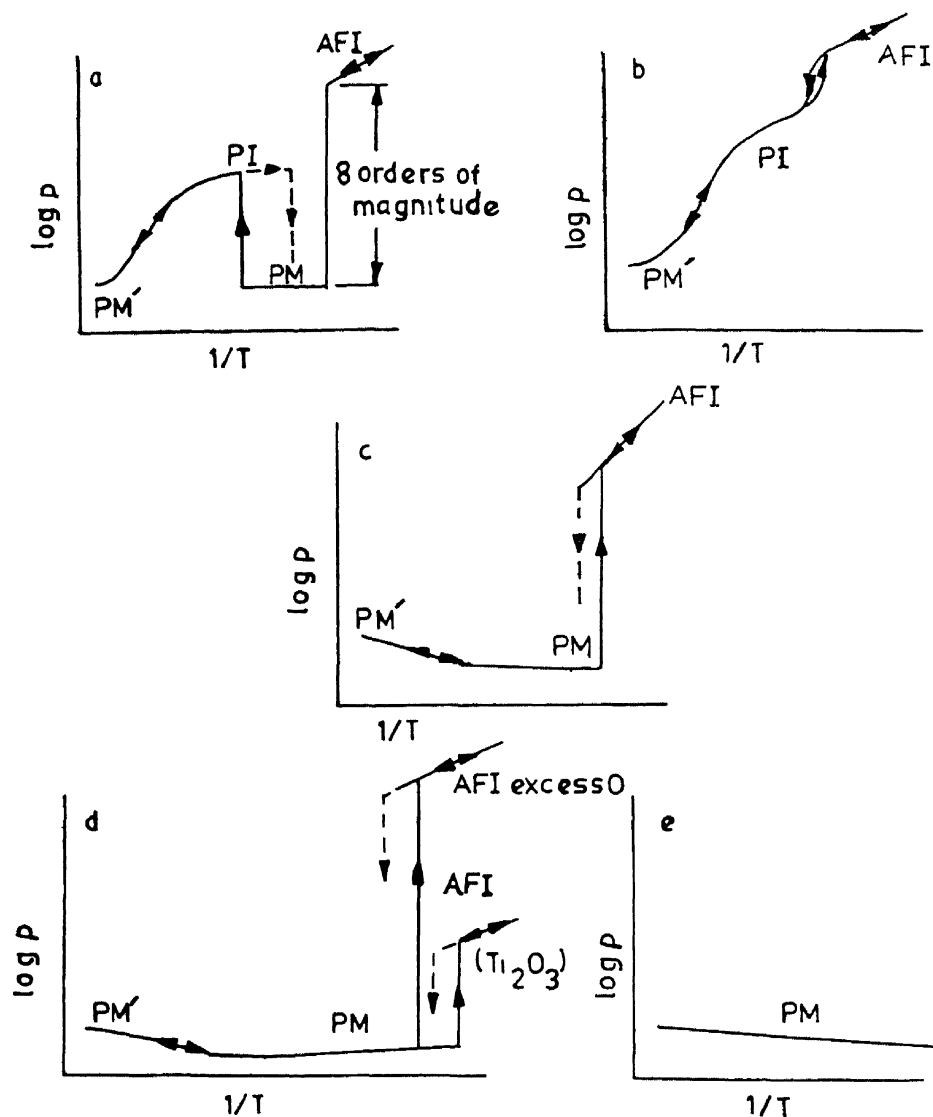


FIG 1 Schematic diagram depicting the changes of resistivity ρ with temperature T for the V_2O_3 alloy system. Part (a): $(V_{1-x}Cr_x)_2O_3$ with $0.005 < x < 0.018$, note the three transitions $AFI \rightarrow PM \rightarrow PI \rightarrow PM'$ with rising T and the large hysteresis involved in the $PM \rightarrow PI$ transformation. Part (b): $(V_{1-x}Cr_x)_2O_3$ with $x > 0.018$, the metallic PM phase is now bypassed. Part (c): Undoped V_2O_3 , the PM - PI transition is bypassed. Part (d): $(V_{1-x}Ti_x)_2O_3$ for $0 < x < 0.055$ and $(V_{1-y}\square_y)_2O_3$ $0 < y < 0.009$, this situation is similar to part (c) but the transition is shifted to lower temperatures and the size of the AFI - PM discontinuity in $\log \rho$ is altered. Part (e): $(V_{1-x}Ti_x)_2O_3$ for $x > 0.055$ and $(V_{1-y}\square_y)_2O_3$ for $y > 0.009$, the alloys remain metallic.

rather complex set of transitions. The principal feature of interest is the fact that a causal factor as small as thermal energy change of the order of $k_B T$ (where k_B is the Boltzmann constant and T , the temperature) can bring about repercussions that are all out of proportion to the stimulus. It will be our task to explore these matters in the subsequent sections. In particular, we focus on the problem of rationalizing the observed reentrant metallic behaviour of the $(V_{1-x}Cr_x)_2O_3$ alloys with $0.005 < x < 0.018$.

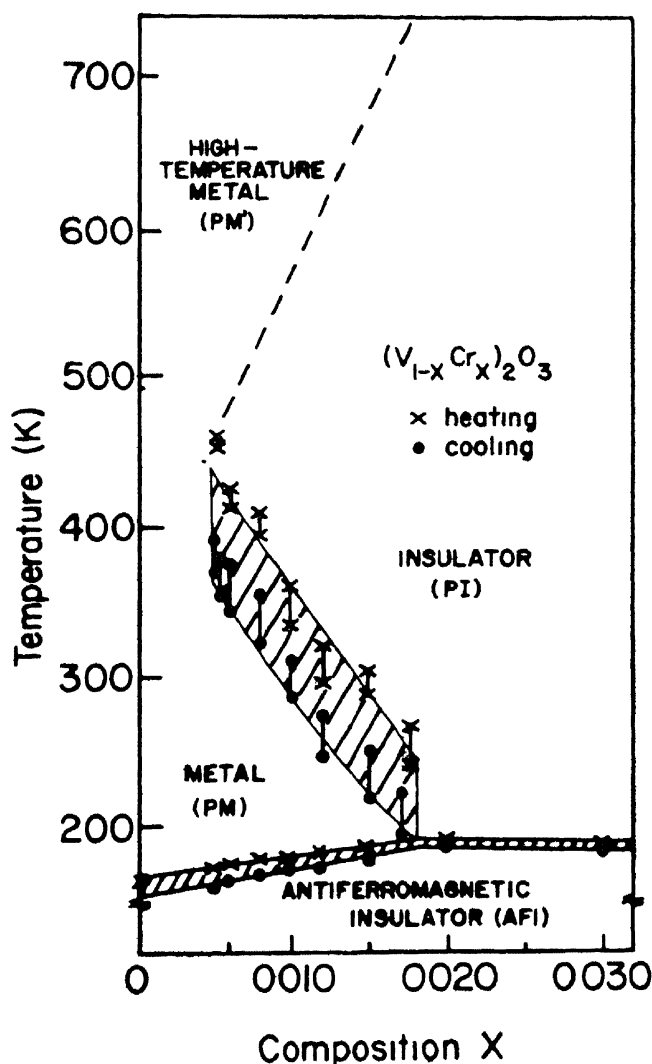


FIG 2 Experimental phase diagram for the $(V_{1-x}Cr_x)_2O_3$ alloys system. Hatched areas show ranges of hysteretic effects. Dotted line separating PM and PM' regions is drawn at midpoint of the gradual transition

II THEORETICAL INTERPRETATION

A Historical Survey

There have been many attempts to explain the rich variety of transitions encountered in the V_2O_3 alloy systems. In many instances models were proposed before an adequate data base had become available, and a number of such descriptions are no longer tenable.

Many of the proposed mechanisms are couched in rather equalitative terms. Among these are the adoption by the Bell group^{5,9} of electron correlations as the principal driving mechanism for one or more of the observed transformations, thus the several phase changes were classified by them as examples of the Mott transition¹⁵⁻¹⁹. On the other hand, the Purdue group^{14,15} has pointed to unmistakable signs that the lattice also plays an important role in the transitions, they inter-

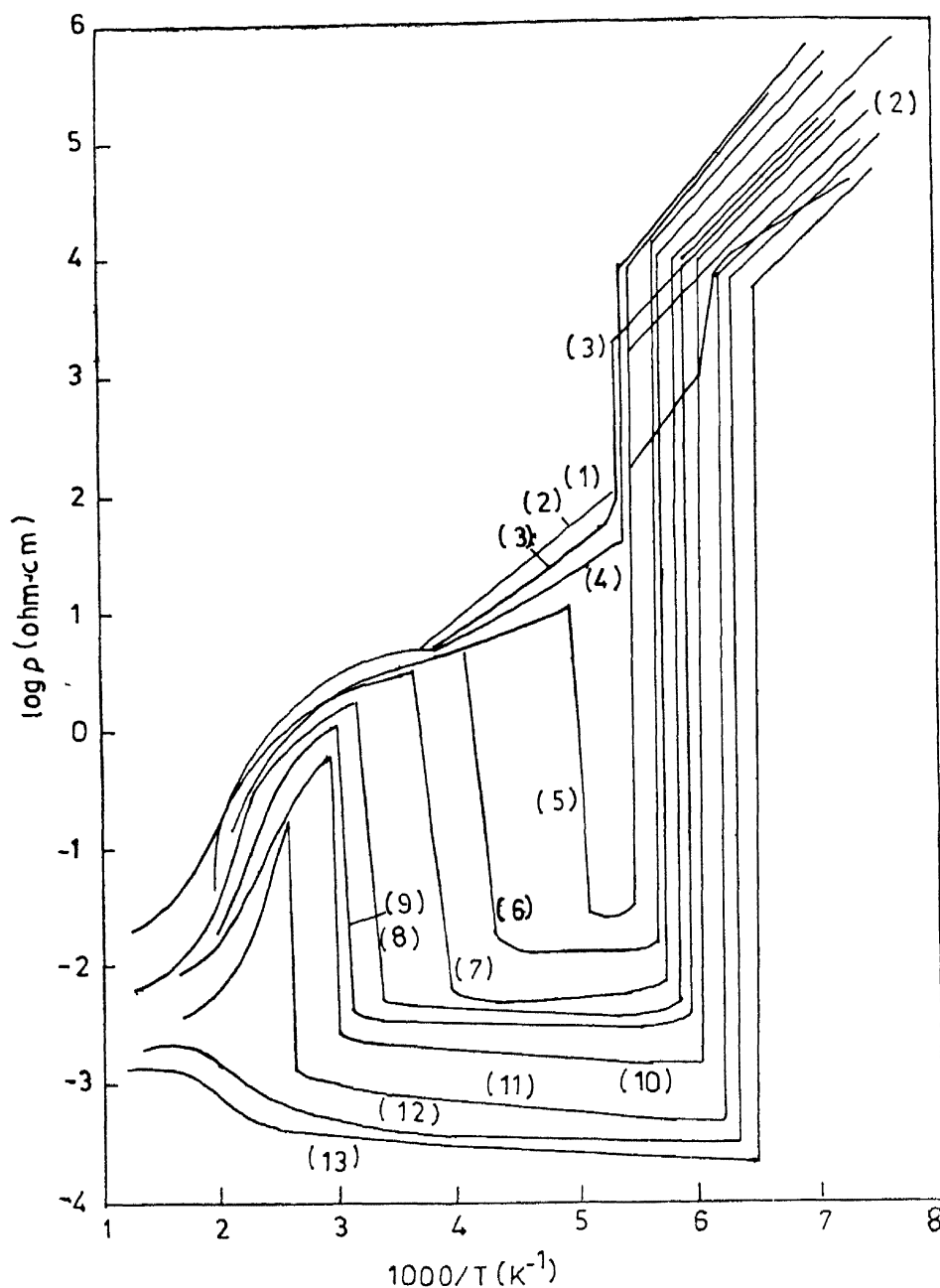


FIG 3 Experimental measurements pertaining to the variation of resistivity ρ with temperature T for the V_2O_5 alloy system. Part (a). $(V_{1-x}Cr_x)_2O_5$ with $0 \leq x \leq 0.1$, note the varying number of metal-insulator transitions for the regimes $0 \leq x < 0.005$, $0.005 < x < 0.018$, and $0.018 < x < 0.10$

preted their data in terms of the density-of-states [DOS] diagram peculiar to the states of primarily d -character in V_2O_5 .¹⁴ They emphasized that the Fermi level was situated in a deep minimum of the DOS, which can be opened up and closed again by small perturbations on the system.

In a later Section, we will present a theory that in a sense mediates between these opposing views and which seems to provide a more adequate interpretation of the experimentally observed phase diagram of Fig. 2.

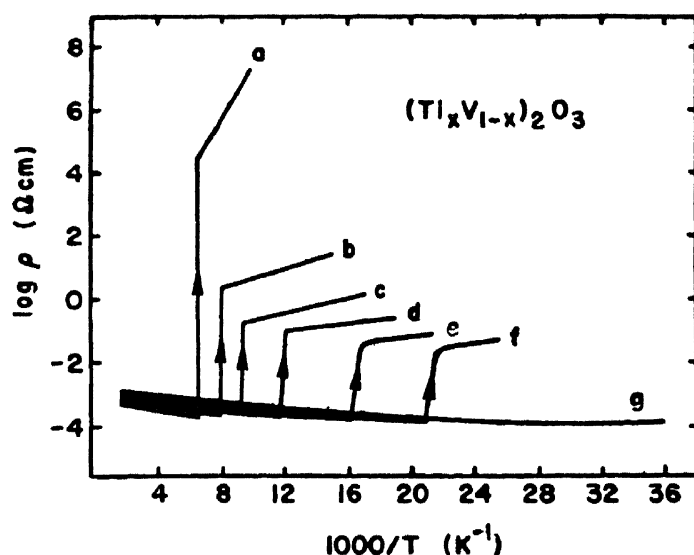


FIG 3 Part (b) : $(V_{1-x}Ti_x)_2O_3$ for $0 < x < 0.015$, note the reduction in conductivity activation energy and the diminution of the resistivity discontinuity with increasing x .

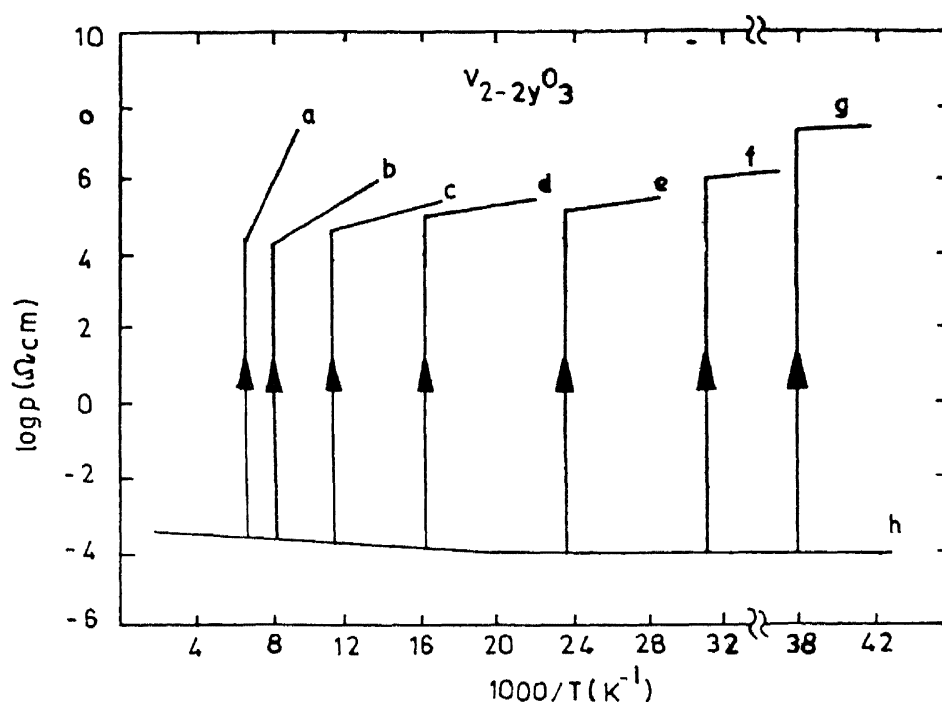


FIG 3 Part (c) : $(V_{1-y})_2O_3$ note the variation of conductivity activation energy and of the discontinuity in resistivity with increasing y

Aside from the above qualitative formulations, several quantitative theories have been advanced. Among these is the treatment by Brinkman and Rice²¹, they studied the mechanism of metal-insulator transitions at the absolute zero of temperature ($T = 0$) in terms of electron correlation effects whose strength was specified by the ratio U/W , where U is the intra-atomic Coulomb repulsion energy for the electrons situated on the same lattice site, and W is the bare-particle band width. This theory applies to phenomena as observed when one moves along the abscissa

of the phase diagram in Fig. 2 at $T = 0$, but which was not extended to the regime of non-zero temperature. The Brinkman-Rice analysis, therefore, is primarily applicable to experiments in which either the concentration of additives to the V_2O_3 host is altered or in which pressure changes are studied, as shown later, both these effects scale roughly linearly with U/W . It may also be shown²² that the above theoretical formulation is recovered as a special case of the treatment described below.

Several theories, describing the phase transitions of V_2O_3 at non-zero temperatures have also been published. Cyrot^{23,24} constructed a phase diagram that summarized the various transition anticipated for the system. To obtain first-order transformations he found it necessary to include a volume-dependence of the bare bandwidth W , in addition to magnetic spin fluctuations. His phase diagram in the $k_B T/W$ vs. U/W plane is only in rough conformity with the various phases experimentally detected in the V_2O_3 system. Moriya and Hasegawa²⁵ as well as Hasegawa²⁶ have applied spin fluctuation theory to the problem, they did not obtain any first-order transition, which fact they attributed to neglect of lattice effects.

As an alternative, Zeiger²⁷ proposed a theory in which electron correlation effects compete against the entropy of electrons in band states. He allowed the one electron energies to depend on interatomic separations. The five parameter theory and specification of density-of-state (DOS) functions for two bands can explain a large variety of experimental results in the V_2O_3 alloy system but is less successful in dealing with detailed electrical properties.

Several theories of the band structure for the V_2O_3 alloy systems have also been published²⁸⁻³¹. While differing in detail all treatments yield DOS curves for the d -band in which sharp peaks and deep valley alternate. In such circumstances, if the Fermi level coincides with a valley, small external perturbations such as magnetic ordering effects, application of pressure, changes in temperature, and variations in alloy-composition are sufficient to open up or close a band-gap that takes the place of the minimum in the DOS curve. In these models correlation effects play a somewhat subsidiary role, but they are still manifest in the small widths of the subbands.

Another approach was introduced simultaneously by Minesaki,³² Ramirez *et al*³³ and by Alascio *et al*³⁴ who essentially adapted the order-disorder theory, as elaborated upon by Falicov and Kimball³⁵ to electrons and holes in localized and itinerant states. These authors calculated the fraction of carriers available for electrical conduction as a function of temperature in terms of an electron-hole interaction energy parameter, they found a very sharp change in carrier density with temperature, beyond a critical value of the interaction energy. This is a manifestation of the metal-insulator transition. The latter is driven jointly by the electron-hole interactions, by the configurational entropies arising from the distribution of electrons among the two levels of each lattice site, and by alterations in magnetic spin entropy resulting from changes in electron population on each site. The principal difficulty with this approach is that, without further modification, it does not provide an explanation of the reentrant metallic behaviour encountered in the V_2O_3 alloy system.

We now present in outline form a recent theoretical development^{22,36} that mediates between the strongly correlated electron limit and freely itinerant electron behaviour. As will be seen, the simple approach developed here rather successfully deals with the observed variety of electrical properties of the V_2O_3 alloy system; however, lattice effects which have been neglected must be built in at a later stage to obtain a more satisfactory representation of experimental data.

III ELEMENTARY DESCRIPTION OF THE CORRELATED PARAMAGNETIC REGIME

A. Preliminaries

The task of providing a theoretical framework for interpreting the reentrant metallic characteristics of the V_2O_3 alloy system will be attended to in several stages of increasing complexity. We recognize at the outset that even in the metallic phase electrons in bands of primarily d -character are strongly correlated, this interaction must be included in the expressions for both the band (kinetic) energy of the charge carriers and for the potential interaction energies. To simplify the analysis we assume that electrons are accommodated in a single, non-degenerate band that is exactly half-filled; we, later, specialize to the limiting case of low temperatures ($T \rightarrow 0$). Our approach is to provide first a phenomenological description of the electronic states by deriving expressions for the Helmholtz free energy F of the charge carriers either in the paramagnetic metallic (PM) or in the paramagnetic insulating (PI) regimes. A transition between these states is achieved when the coexistence line $F_{PM} = F_{PI}$ is crossed in either direction by alteration of temperature or of sample composition.

B. The Potential Energy of Interaction in the Metallic Regime

The potential interaction energy among correlated electrons will be handled in a very elementary manner along the lines suggested by Hubbard.²⁰ The charge carriers are treated as non-interacting unless two of them settle on the same lattice site with opposing spins, in which case their interaction energy is set equal to U . The total potential energy is thus given by $U\eta$, where η is the expectation value $\langle n_{j\uparrow}n_{j\downarrow} \rangle$ for encountering a typical site in a doubly occupied state, involving two electrons with opposing spins. In the PM regime $\langle n_{j\uparrow} \rangle$ and $\langle n_{j\downarrow} \rangle$ are assumed to be independent of the site index j .

C. The Kinetic Energy of the Correlated Electron Gas

The potential energy of interaction described above also produces a hindered motion whenever the charge carriers attempt to get past each other. An elementary technique for dealing with this problem is to construct a set of independent quasiparticles of band energy E that take the place of the interacting electrons. The central *ansatz* in the present theory is that the energy of quasiparticles E is related to the bare particle energy ϵ by a universal scaling law of the form $E = \Phi(\eta)\epsilon$, where the factor Φ depends functionally on η but is independent of temperature T . The rationale for such a step is explained elsewhere²² in some detail, but ultimately its adoption can only be justified by the degree of success one achieves in dealing with

complicated experimental observations. The band energy of the N quasiparticles may now be written as

$$\frac{E_B}{N} = \int_{-\infty}^{\infty} E f(E) \rho(E) dE, \quad \dots(1)$$

where $f(E) \equiv f[(E - E_F)/k_B T]$ is the Fermi-Dirac distribution function for the quasiparticles (E_F is the Fermi energy), and $\rho(E)$ is the appropriate density-of-states (DOS) function. Next, introduce the scaling law, one then finds that $f(E) \equiv f[(E - E_F)/k_B T] = f[\Phi(\epsilon - \mu)/k_B T] = f[(\epsilon - \mu)/k_B T^*] \equiv f^*(\epsilon)$ in which we have set $\mu \equiv E_F/\Phi$ as the Fermi energy for bare particles and $T^* \equiv T/\Phi$ as an *effective temperature*. As regards the DOS, by definition, $\rho(E)$ is proportional to a set of Dirac delta distributions $\delta(E - E_{\mathbf{k}})$ centered on each of the allowed eigenvalues $E_{\mathbf{k}}$ of the quasiparticle energy spectrum. Thus,

$$N\rho(E) = \sum_{\mathbf{k}} \delta(\Phi(\epsilon - \epsilon_{\mathbf{k}})) = \sum_{\mathbf{k}} \Phi^{-1} \delta(\epsilon - \epsilon_{\mathbf{k}}) = \Phi^{-1}(\eta) \rho_0(\epsilon) N; \quad \dots(2)$$

that is, the DOS for the quasiparticle $\rho(E)$ and bare particle systems $\rho_0(\epsilon)$ are related by the scaling factor Φ . Lastly, we replace E and dE in terms of ϵ and $d\epsilon$. Eq (1) thus becomes

$$\frac{E_B}{N} = \Phi \int_{-W/2}^{W/2} \epsilon f^*(\epsilon) \rho_0(\epsilon) d\epsilon \equiv \Phi(\eta) \bar{\epsilon}(T^*) \quad (3)$$

We see that the band energy for a set of quasiparticles (and through the ansatz, the interacting electron system) can be handled by introducing the kinetic energy of an equivalent set of noninteracting electrons at an effective temperature T^* , multiplied by a band-narrowing factor $\Phi < 1$ (see below).

D The Energy of the Correlated Electron System in the Paramagnetic Regime

We next combine the preceding results to obtain a total band energy in the form

$$\frac{E_{PM}}{N} = \Phi(\eta) \bar{\epsilon}(T^*) + U_{\eta} \quad \dots(4)$$

It is now necessary to specify the functional form $\Phi(\eta)$. This problem has been dealt with elsewhere²² and will not be discussed in detail. For a half-filled band, $\eta \leq 1/4$, one, therefore, assumes that Φ may be expanded in a Taylor series of the form $\Phi = f_0 + f_1\eta + f_2\eta^2 + \dots$, the f_i multipliers are then found by requiring E_{PM} to coincide with certain limiting cases for which the total energy is well established. This procedure leads to the simple expression, valid for a half-filled band,

$$\Phi(\eta) = 8\eta(1-2\eta) \quad \dots(5)$$

Finally, to explore the low-temperature limiting value of E_{PM} we adopt the featureless DOS of rectangular character for $-W/2 \leq \epsilon \leq W/2$, $\rho_0(\epsilon) = 2/W$;

outside this range $\rho_0(\epsilon)$ vanishes. Then for a half-filled band we can set $f^*(\epsilon) = 1$ inside the range $-W/2 \leq \epsilon \leq 0$ and set $f^*(\epsilon) = 0$ elsewhere. For this case eq (2) yields $\bar{\epsilon}(0) = -W/4$, so that

$$\frac{E_{PM}}{N} = -\left(\frac{W}{4}\right)\Phi + U\eta \quad \dots(6)$$

Consistent with the limit of low temperatures and the use of quasiparticles that obey Fermi-Dirac statistics we now adopt the Sommerfeld approximation for the electronic heat capacity C of the quasiparticles :

$$C = \gamma(E_F)T; \quad \gamma = \frac{2}{3} \pi^2 \rho^\sigma(E_F) = \frac{2}{3} \frac{\pi^2 \rho_0^\sigma(\epsilon)}{\Phi} k_B^2 \equiv \frac{\gamma_0}{\Phi}, \quad \dots(7)$$

where we have introduced the Sommerfeld constant γ for the quasi-particles and then transformed to the expression γ_0 appropriate to bare particles. The energy and entropy are now given as

$$\frac{E_{PM}(T)}{N} = -\left(\frac{W}{4}\right)\Phi + U\eta + \int_0^T C dT = -\left(\frac{U}{W}\right)\Phi + U\eta + \frac{\gamma_0 T^2}{2\Phi} \quad \dots(8a)$$

$$\text{and} \quad \frac{S_{PM}(T)}{N} = \int_0^T \left(\frac{C}{T}\right) dT = \frac{\gamma_0 T}{\Phi} \quad \dots(8b)$$

E. The Free Energy Functional for the Correlated Metallic Phase and its Minimization

One may now construct the Helmholtz free energy functional as $F_{PM} = E_{PM} - TS_{PM}$, from (8) one finds

$$\frac{F_{PM}}{N} = -\left(\frac{W}{4}\right)\Phi + U\eta - \frac{1}{2} \frac{\gamma_0 T^2}{\Phi} \quad \dots(9)$$

It should be carefully noted that the above is not the Helmholtz free energy, because it contains the extrathermodynamic variable η and the function $\Phi(\eta)$ thereof. We thus utilize the Landau technique by minimizing F_{PM} with respect to η using eq (5). The condition $(\partial F_{PM}/\partial \eta) = 0$ in the limit $T \rightarrow 0$ yields

$$\eta = \eta_0 = \frac{1}{4} \left(1 - \frac{U}{2W}\right) \quad \dots(10a)$$

$$\Phi = \Phi_0 = 1 - \left(\frac{U}{2W}\right)^2 \quad \dots(10b)$$

and when these quantities are inserted in (9) one obtains the final result

$$\frac{F_{PM}}{NW} = -\frac{\Phi_0}{4} + \frac{U}{W} \eta_0 - \frac{\gamma_0 T^2}{2\Phi_0 W} \quad (11)$$

Actually, we have been slightly inconsistent in the above approach we should have retained in eqs (10a) and (10b) terms up to order T^2 , before substituting the expanded expressions for η and Φ into eq (9). However, it turns out that these higher order terms simply cancel out in the final substitution, so that eq. (11) is again recovered when a self-consistent procedure is adopted. The Helmholtz free energy for the paramagnetic phase thus consists of a temperature-independent term associated with the energy

$$\frac{E}{NW} = -\frac{\Phi_0}{4} + \frac{U}{W} \eta_0 = -\frac{1}{4} \left(1 - \frac{U}{2W}\right)^2 \equiv J, \quad \text{.. (12)}$$

and of a temperature-dependent portion $-\gamma_0 T^2/2\Phi_0 W$ associated with the $-TS/NW$ contribution to F/NW .

F. The Free Energy for the Paramagnetic Insulating Phase

We turn now to the formulation of the free energy for the paramagnetic insulating phase. For $n = 1$ the ground state achieved in the low-temperature limit is a distribution of one localized carrier on each site. The energy of this collection coincides with the midpoint of the non-degenerate band described above, i.e. with the assumed zero of energy. Since there are essentially no double occupancies, the repulsive potential energy also vanishes. This leaves only the entropy of the system, given by $Nk_B \ln 2$, since at any given site the electron spin can be in either the spin-up or the spin-down configuration.

Accordingly, the reduced Helmholtz free energy per particle is given by

$$\frac{F_{PI}}{NW} = -\left(\frac{k_B T}{W}\right) \ln 2 \quad (13)$$

G Coexistence Conditions and Phase Diagrams

One can now inquire under what conditions a phase transition from the PM to the PI configuration or its reverse may be achieved. For this purpose one must cross the coexistence line which is defined by the constraint that the chemical potential of the two phases be the same. One must thus set $F_{PM}/NW = F_{PI}/NW$; on equating eqs. (11) with (13) one obtains a quadratic equation in $k_B T/W$ which may be solved for its two roots

$$\left(\frac{k_B T}{W}\right)_{\pm} = \frac{k_B^2 \Phi}{\gamma_0 W} \left\{ \ln 2 \pm \left[(\ln 2)^2 - \frac{2\gamma_0}{k_B^2} \left(\frac{W}{4} - \frac{U}{\Phi_0} \eta_0\right) \right]^{1/2} \right\} \quad (14)$$

On substituting for γ_0 , Φ_0 , η_0 and setting $\rho_0^{\sigma} = \frac{1}{W}$ for the featureless DOS for a particle of specified spin σ , we finally obtain

$$\left(\frac{k_B T}{W}\right)_{\pm} = \frac{3}{2\pi^2} \left[1 - \left(\frac{U}{2W}\right)^2 \right] \left\{ \ln 2 \pm \left[(\ln 2)^2 - \frac{\pi^2}{3} \frac{(1 - U/2W)}{(1 + U/2W)} \right]^{1/2} \right\} \quad \text{.. (15)}$$

Eq. (15) forms the basis for the construction of the phase diagram in the low-temperature limit, for the case $n = 1$, and for a featureless DOS. The diagram is shown in Fig 4 as a plot of $k_B T/W$ vs U/W . Several features are of interest: There is a lower limit, $(U/W)_1$ below which only the PM phase is encountered at all temperatures. The value $(U/W)_1$ represents the point at which the two solution branches $(k_B T/W)_+$ and $(k_B T/W)_-$ coalesce. The lower branch, $(k_B T/W)_-$ drops away from the coalescence point and reaches zero at $U/W = 2$ on the abscissa. The upper branch rises away from the coalescence point, we have arbitrarily cut it off well below the value $U/W = 1.765$ which is a true, automatic cut-off point in the more sophisticated approach cited below. One must remember that for reduced temperatures $k_B T/W$ considerably in excess of the coalescence point the low-temperature approximation fails, and unphysical predictions ensue if one pushes the theory too far beyond that point.

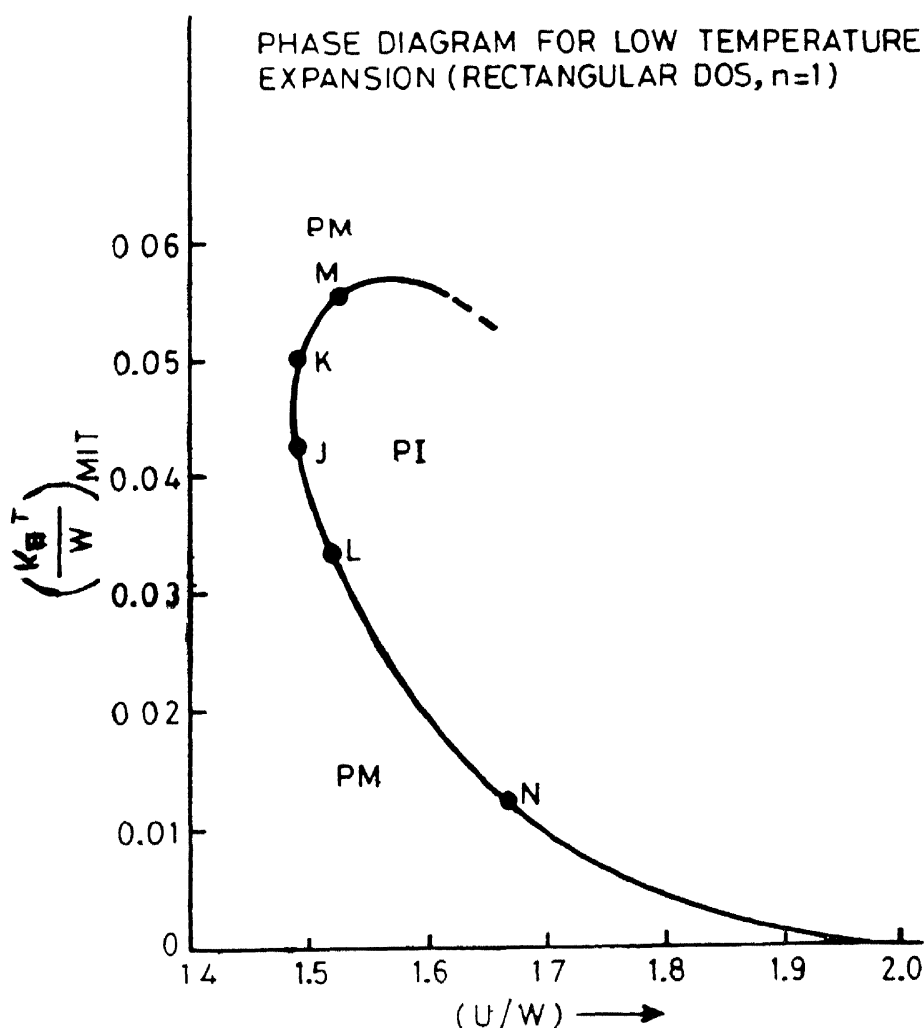


FIG 4 Theoretical phase diagram for the coexistence of metallic and insulating states of a paramagnetic material characterized by a single band that is exactly half-filled. Note the extent of the stability ranges for the PM, PI and PM' configurations. The phase diagram was determined in the low-temperature limit discussed in the text, the upper critical point is arbitrarily placed as shown (see text). The labels J, K, L, M, N correspond to those of Fig. 5.

The origin of the phase diagram may readily be understood by comparing eqs. (11) with (13). The expression for the reduced free energy of the PI phase forms a straight line passing through the origin on a F/NW vs $k_B T/W$ plot, as shown by trace (e) in Fig 5. By contrast, the corresponding expression for the PM phase forms a parabola with a negative intercept J as specified by eq (12), and a curvature, both of which depend on U and W . For small U/W , i.e. when correlation effects are minor, J is numerically large, the resulting parabola, sketched as curve (a) in Fig 5, everywhere lies below (e). The free energy for the PM phase is always less than that of the PI configuration, no transition occurs, and only the mildly correlated metallic phase is encountered. As U/W increases, J becomes numerically smaller and the intercept rises. This ultimately places the parabola up sufficiently high on the ordinate scale that it can cut the straight line (e) at two points, denoted by JK or LM for representative curves (b) or (c) respectively. These intersection points are also marked in Fig 4. In these circumstances the metallic and insulating phases alternate in exhibiting the lower free energy. As the temperature rises one encounters the progression $PM \rightarrow PI \rightarrow PM'$ which mimics the reentrant metallic feature seen for certain V_2O_5 alloys as described earlier. Finally, as J becomes numerically small the parabola intersects the straight line only at one point N , as illustrated for traces (d) and (e) in Fig 5. The second intersection point occurs at unphysical temperatures. Point N is also entered in Fig. 4. In this regime only the $PM \rightarrow PI$ transformation occurs with rising temperatures.

In summary, a very simple electron correlation model has been proposed to provide a qualitative rationalization of the phase diagram for the paramagnetic configuration of materials characterized by various values of U/W . It should be

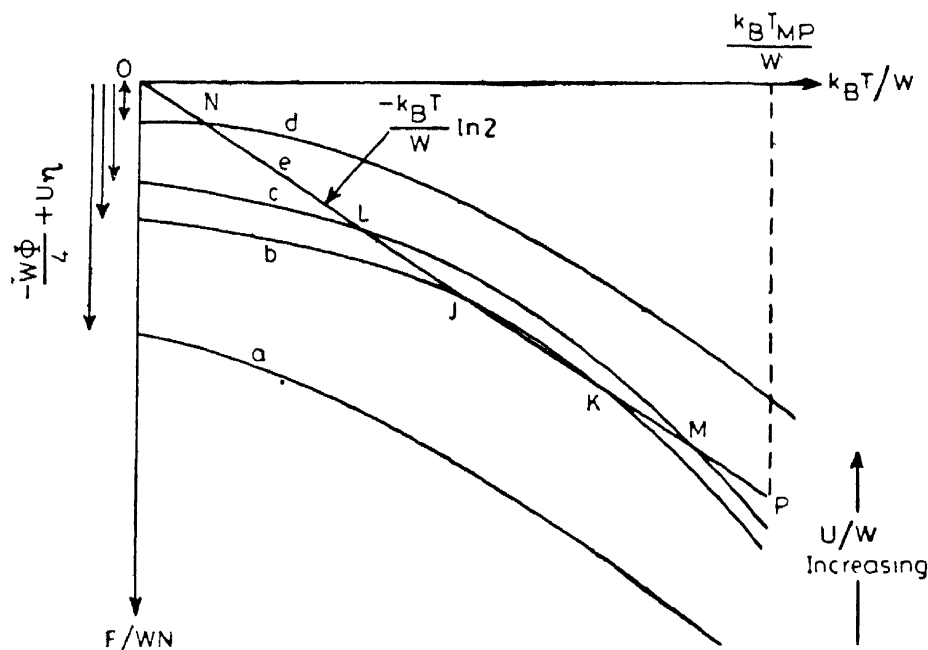


FIG 5 Plots of eqs (11) and (13) for different values of the U/W parameter. Note the points of intersection JK, LM, N and their counterpart in Fig 4

noted that the succession of phases described above is achieved for *fixed* U/W simply by varying the temperature. That such small doses of energy input can achieve such drastic changes in electron configuration is due to the fact that, under conditions where the negative band energies and positive electron correlations nearly balance, the much smaller entropy effects are the deciding factor whether the electrons are in an insulating or metallic state.

We shall defer a comparison between theory and experiment until the more complete theory has been developed below.

IV IMPROVED THEORY OF CORRELATED ELECTRON STATES FOR PARAMAGNETIC MATERIALS

A. *Introductory Comments*

The preceding treatment of electron correlation effects is rather primitive and needs to be placed on a sounder theoretical footing. This we accomplish by setting up a theory which deals with the PM or PI phase for both of which itinerant and localized electrons are postulated to coexist. Their ratio must then be adjusted self-consistently by minimizing the functional $F(\eta)$ constructed from the energy and entropy contribution as described below. Naturally, the resulting analysis is now more complex and must ultimately be carried out numerically. By way of compensation we can drop the restriction of operating in the low-temperature limit.

From quite general considerations it may be shown that, for very large intra-atomic repulsion energies U , Φ represents the conditional probability that an electron will execute a transition to a neighbouring site if the latter is empty. For very large U such a transition is prohibited if the neighbouring site is already occupied by another electron. This makes it plausible to associate with Φ the fraction of itinerant electrons, i.e. those capable of executing a transition to other sites; $(1 - \Phi)$ then represents the fraction of electrons hemmed in (i.e. localized) by the lack of available unoccupied nearest neighbor sites. This association holds even for U values which are no longer large compared to bare particle band widths W , in the limit $U \rightarrow 0$ the entire question is academic since then all electrons are itinerant.

B. *The Energy of the Electron Assembly*

To obtain the energy of the electron assembly we proceed in strict analogy to the procedure described in Sec. III C. We replace the interacting electrons, whether itinerant or localized, by a quasiparticle assembly of energy $E_B = \sum_{(\mathbf{k})} E_{\mathbf{k}} f(E_{\mathbf{k}})$ where the summation extends over all quantum states occupied by the representative quasiparticles. We then switch to an integration after introducing the DOS $\rho(E)$ and the same scaling law $E = \Phi\epsilon$ as before. This immediately yields

$$\frac{E}{N} = \Phi \int_{-W/2}^{W/2} \epsilon \rho_0(\epsilon) f^*(\epsilon) d\epsilon + U\eta \quad \dots(16)$$

as the total energy of the interacting electron assembly

On introducing the explicit form for the Fermi-Dirac function as in Sec. IIIC, we obtain

$$\frac{E}{N} = \Phi \int_{-W/2}^{W/2} d\epsilon \epsilon \rho_0(\epsilon) \tanh\left(\frac{\epsilon}{2k_B T^*}\right) + U\eta \quad (17)$$

and on substituting $\rho_0(\epsilon) = 2/W$ and carrying out the integration we find

$$\frac{E}{NW} = \frac{2k_B T}{W} \left\{ \int_0^1 dx \ln \cosh\left(\frac{W\Phi x}{4k_B T}\right) - \ln \cosh\left(\frac{W\Phi}{4k_B T}\right) \right\} + \frac{U\eta}{W} \quad (18)$$

The zero of entropy for the electrons has been chosen so as to coincide with the entropy of the localized electron assembly

C The Entropy Contribution of the Electron Assembly

In considering the entropy of electrons we must recognize two distinct contributions: the thermal entropy of mobile carriers, weighted by the factor Φ and the configurational entropy of localized carriers associated with a weighting factor $(1 - \Phi)$.

The entropy of the itinerant electron assembly as represented by the quasiparticles is specified by

$$\frac{S_i}{N} = - \left(\frac{\Phi k_B}{N} \right) \sum_{\mathbf{k}\sigma} \{ f(E_{\mathbf{k}}) \ln f(E_{\mathbf{k}}) + [1 - f(E_{\mathbf{k}})] \ln [1 - f(E_{\mathbf{k}})] \} \quad (19)$$

On switching to an integration over $E_{\mathbf{k}}$ involving the DOS $\rho(E_{\mathbf{k}})$ and then transforming to the bare particle energies as described earlier we obtain

$$\frac{S_i}{N} = - \Phi k_B \int_{-W/2}^{W/2} d\epsilon \rho_0(\epsilon) \{ f^*(\epsilon) \ln f^*(\epsilon) + [1 - f^*(\epsilon)] \ln [1 - f^*(\epsilon)] \} \quad (20)$$

After inserting the expression for $f^*(\epsilon)$ the above expression becomes

$$\begin{aligned} \frac{S_i}{N} = \Phi k_B \left\{ 2 \ln 2 - \int_0^{W/2} d\epsilon \rho_0(\epsilon) \left[\frac{\epsilon}{k_B T^*} \tanh\left(\frac{\epsilon}{2k_B T^*}\right) \right. \right. \\ \left. \left. - 2 \ln \cosh\left(\frac{\epsilon}{2k_B T^*}\right) \right] \right\} \quad (21) \end{aligned}$$

On introducing the usual featureless DOS function we obtain the final relation

$$\frac{S_1}{N} = \Phi k_B \left\{ 2 \ln 2 - 2 \ln \cosh \left(\frac{W\Phi}{4k_B T} \right) + 4 \int_0^1 dx \ln \cosh \left(\frac{W\Phi x}{4k_B T} \right) \right\} \quad (22)$$

The entropy of the localized electron group is calculated according to the expression

$$\frac{S_1}{N} = (1 - \Phi) k_B \sum_j P_j \ln P_j \quad (j = 0, 1, 2, 3), \quad (23)$$

where the P_j specify the probability that a given lattice site contains no electron, a localized electron in spin-up or spin-down configuration, or two electrons of opposite spin. The probabilities are listed in Table I, on introducing the condition $v_\sigma = v_{-\sigma} = v/2$ for the paramagnetic regime and the particle conservation law $n = v + 2\eta$, the entropy for the localized phase is specified as

TABLE I

Configuration	Designation	Average Probability of Occurrence
Site Contains Electron with Spin Up $\sigma = 1$	P_2	v_σ
Site Contains Electron with Spin Down; $\sigma = -1$	P_3	$v_{-\sigma}$
Doubly Occupied Site	P_4	η
Unoccupied Site	P_1	$1 - v - \eta$

$$\left(\frac{S_1}{N} \right) = k_B (1 - \Phi) [- (n - 2\eta) \ln (n - 2\eta) + (n - 2\eta) \ln 2 - \eta \ln \eta - (1 - n + \eta) \ln (1 - n + \eta)] \quad (24)$$

D. The Free Energy of the System

The Helmholtz free energy is given by $F(\eta) = E(\eta) - T[S_1(\eta) + S_2(\eta)]$ as specified by eqs (18), (21), and (24). For simplicity we now specialize to the case of the half-filled band, $n = 1$. We then find

$$\begin{aligned} \frac{F(\eta)}{WN} = & - \left(\frac{2k_B T}{W} \right) (1 - \Phi) \ln \cosh \left(\frac{W\Phi}{4k_B T} \right) - \left(\frac{2k_B T}{W} \right) \Phi \ln 2 \\ & - \left(\frac{2k_B T}{W} \right) \left[(2\Phi - 1) \int_0^1 dx \ln \cosh \left(\frac{W\Phi x}{4k_B T} \right) \right] + \left(\frac{U}{W} \right) \eta \\ & - k_B T (1 - \Phi) \left\{ (1 - 2\eta) \ln \left[\frac{2}{(1 - 2\eta)} \right] - 2\eta \ln \eta \right\} \quad (25) \end{aligned}$$

in which

$$\Phi(\eta) = 8\eta(1 - 2\eta) \quad (26)$$

Clearly, the above expression is a functional in the extrathermodynamic variable η . We obtain the actual free energy by minimizing the functional through the constraint $\partial F(\eta)/\partial \eta = 0$. This provides the following condition on η —

$$\begin{aligned} & \left(\frac{2k_B T}{W} \right) \left(\frac{\Phi'}{\Phi} \right) (1 - \Phi) \ln \cosh \left(\frac{W\Phi}{4k_B T} \right) - \left[(1 - \Phi) \frac{\Phi'}{2} \right] \tanh \left(\frac{W\Phi}{4k_B T} \right) \\ & - \left(\frac{2k_B T \Phi'}{W} \right) \ln 2 - \left(\frac{2k_B T}{W} \right) \left(\frac{\Phi'}{\Phi} \right) \int_0^1 dx \ln \cosh \left(\frac{W\Phi x}{4k_B T} \right) \\ & + \left(\frac{k_B T \Phi'}{W} \right) \left[(1 - 2\eta) \ln \left(\frac{2}{(1 - 2\eta)} \right) - 2\eta \ln \eta \right] \\ & + \left[2k_B T \frac{(1 - \Phi)}{W} \right] \ln \left(\frac{2\eta}{(1 - 2\eta)} \right) + \frac{U}{W} = 0 \end{aligned} \quad (27)$$

This expression specifies the local extremum $\eta = \eta(k_B T/W, U/W)$ of the free energy F , which is found by substitution of the extremum point into eq. (25).

Obviously, numerical techniques are required to obtain specific predictions. We briefly cite some of the results below.

E. Numerical Predictions Concerning Double Occupancies

The fraction of doubly occupied sites η is a measure of the equilibrium density of charge carriers per site available for charge transport, since on the average there is one electron per site for $n = 1$. Eq. (27) is used to determine $\log \eta$ as a function of $W/k_B T$ for various choices of U/W . The results are shown in Fig. 6 as a plot of $\log \eta$ vs $W/k_B T$. As is seen, η varies only very slightly with T for $1.5 \leq U/W \leq 1.64$ and remains at a value close of 5×10^{-2} , so that $\Phi \simeq 0.4$, the material is a correlated metal. For $1.646 < U/W < 1.765$, the system undergoes two first order changes consistent with reentrant metallic characteristics. In an intermediate temperature range the material displays semiconducting characteristics, the range of stability of the PI phase increases with increasing U/W but the slope of the Arrhenius plot remains essentially unaltered. The corresponding variation just above the critical point (see below) of $U/W = 1.765$ is shown in Fig. 6(b), it is seen that the first-order PI $\rightarrow$ PM' transition at higher temperatures has given way to a smooth transformation from semiconducting to metallic behaviour.

The situation is radically different for $U/W \geq 2$. In this case an Arrhenius plot corresponding to Figs. 6(a) and (b) simply yields a set of straight lines of increasing negative slope and with increasingly negative intercepts as U/W is increased.

F. Thermodynamic Properties of the Correlated Electron System

One can now determine the reduced free energy F/NW from eq. (25) as a function of the reduced temperature $k_B T/W$ for various assumed U/W . The results may be summarized as follows. When $U/W \leq 1.646$ one obtains only one solution

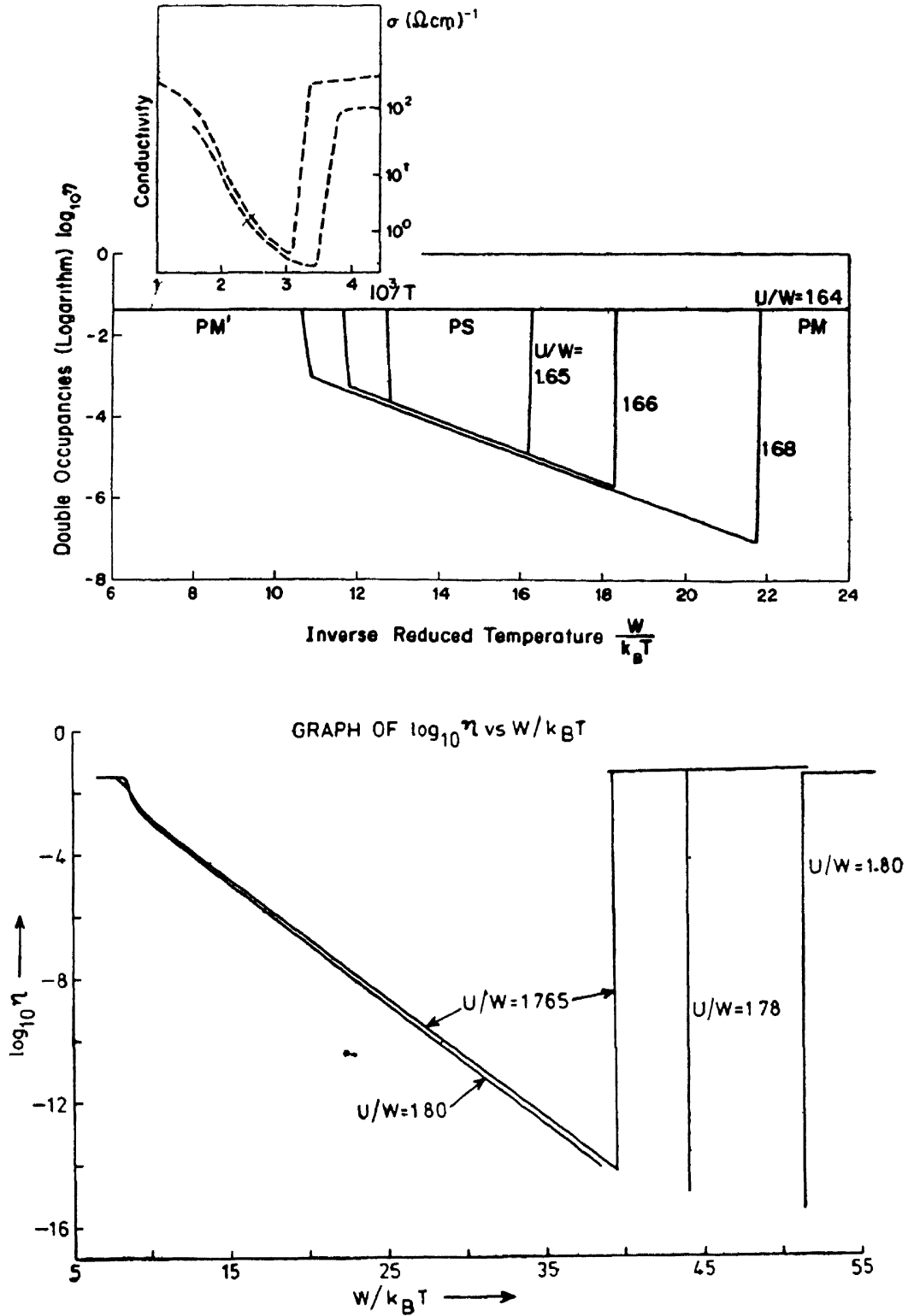


FIG 6 Plots of $\log \eta$ vs $W/k_B T$ as determined via eqs (24) and (25, 26) Part (a) $U/W < 1.646$, note the two sharp electrical transitions and the intermediate PI phase whose domain shrinks as $U/W \rightarrow 1.646$. Inset shows experimental parts of $\log \sigma$ vs $10^3/T$, where σ is the conductivity of $(V_{1-x}Cr_x)_2O_3$ with $x = 0.006, 0.01$. Part (b) U/W slightly in excess of 1.646, note the smooth PI-PM' transition. Calculations performed for a nondegenerate half-filled band, and for a rectangular DOS.

for which F/NW diminishes roughly as $(k_B T/W)^2$ with increasing reduced temperature. For $U/W > 2$ one obtains in first approximation the result $F/WN = -(k_B T/W) \ln 2$. Both these features mirror the results obtained on the basis of the zero order theory.

In the intermediate range of U/W values one generally encounters three solutions for F/NW , of which the lower two must be examined. Obviously, the only stable solution is that for which the reduced free energy is the smallest, but there exists at least one or, over much of the range, two points where crossovers occur, precisely at the values of $k_B T/W$, where η exhibits the discontinuities shown in Fig. 6. These crossing point signal the occurrence of first order phase transformations; from the difference in slope of the free energy curves at the crossovers one can determine the entropy change at the transition using the thermodynamic relation $S = \partial F / \partial T$.

In Fig. 7, we show the phase diagram obtained on the basis of the crossover points described above, these results may be compared with those of Fig. 4. The more sophisticated approach automatically provides a cutoff to the upper branch of the phase boundary which lies above the critical point associated with $(U/W)_{pc}$. At low reduced temperatures the phase boundaries of Figs. 4 and 7 approach each other. The reentrant feature for the paramagnetic regime is again in evidence. For any fixed U/W in the range 1.646 to 1.765, a rise in temperature brings about a succession of changes $PM \rightarrow PI \rightarrow PM'$, the stability range of the PI phase broadens as U/W is increased. For any fixed U/W in the range 1.765 to 2 only the $PM \rightarrow PI$ phase transition is seen. For $U/W > 2$ one encounters a Mott insulator, with $U/W < 1.646$ the material remains in a correlated metallic state.

The entropy changes at the two transition points $PM \rightarrow PI$ and $PI \rightarrow PM'$ are shown in Figs 8(a) and (b) as plots of $\Delta S/k_B N$ vs U/W . These are calculated from the difference in slopes of the corresponding free energy curves at their respective intersection points. It is seen that for both the low and the high temperature transformations the entropy discontinuity at the first order transition reaches a maximum near the midpoint of the U/W range where the transition is encountered.

V MAGNETIC ORDERING EFFECTS

A The Hamiltonian of an Ordered Antiferromagnetic System

We now turn to the description of magnetic ordering effects in strongly correlated electron systems; we then show how to incorporate the essential features into the phase diagram.

We begin with the Hamiltonian for an antiferromagnetically ordered array in which cation subarrays A and B contain atomic constituents with spins oriented in the 'up' and 'down' configurations. The total Hamiltonian may be written as

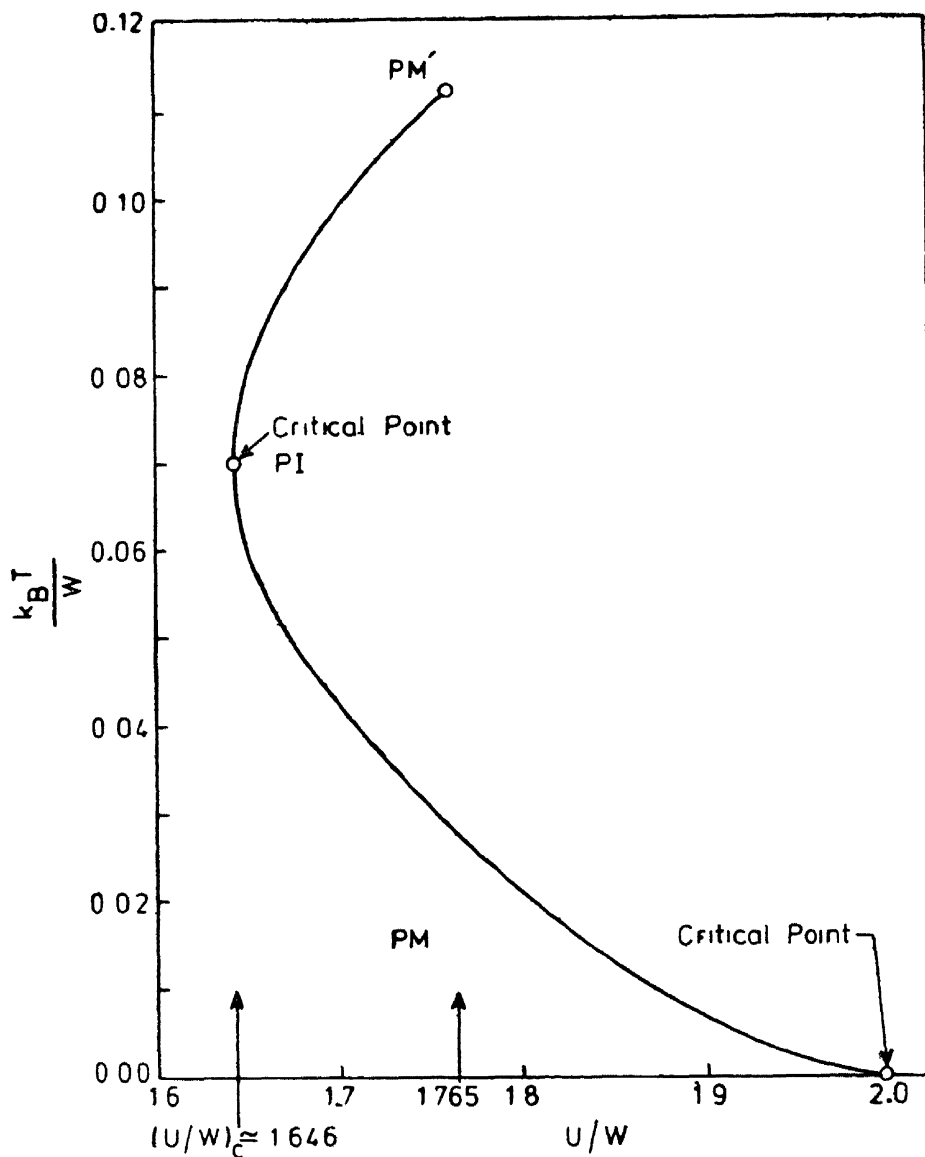


FIG 7 Improved phase diagram, based on the use of eqs (24), (25) and (26), compare with Fig. 4. Calculations carried out for a nondegenerate, half-filled band with a rectangular DOS.

$$\begin{aligned}
 H &= \Phi \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}} n_{\mathbf{k}\sigma} + U\eta + J \sum_{j \in A} \sum_{\substack{j(j) \\ j' \in B}} (S_A, S_{B,j'}) - \left(\frac{1}{4}\right) v_A v_{B,j'} \\
 &= H_B + U\eta + H_{ex}, \quad \dots(28)
 \end{aligned}$$

where the last term on the right is the well-known Anderson exchange term³⁷ with $J = 4t^2(1 - \Phi)/U$. As usual, we restrict the site summation j' to nearest neighbour pairs, S is a spin operator.

We proceed immediately to the mean-field approximation (derived from the assumption that $[a - \langle a \rangle][b - \langle b \rangle] \simeq 0$)

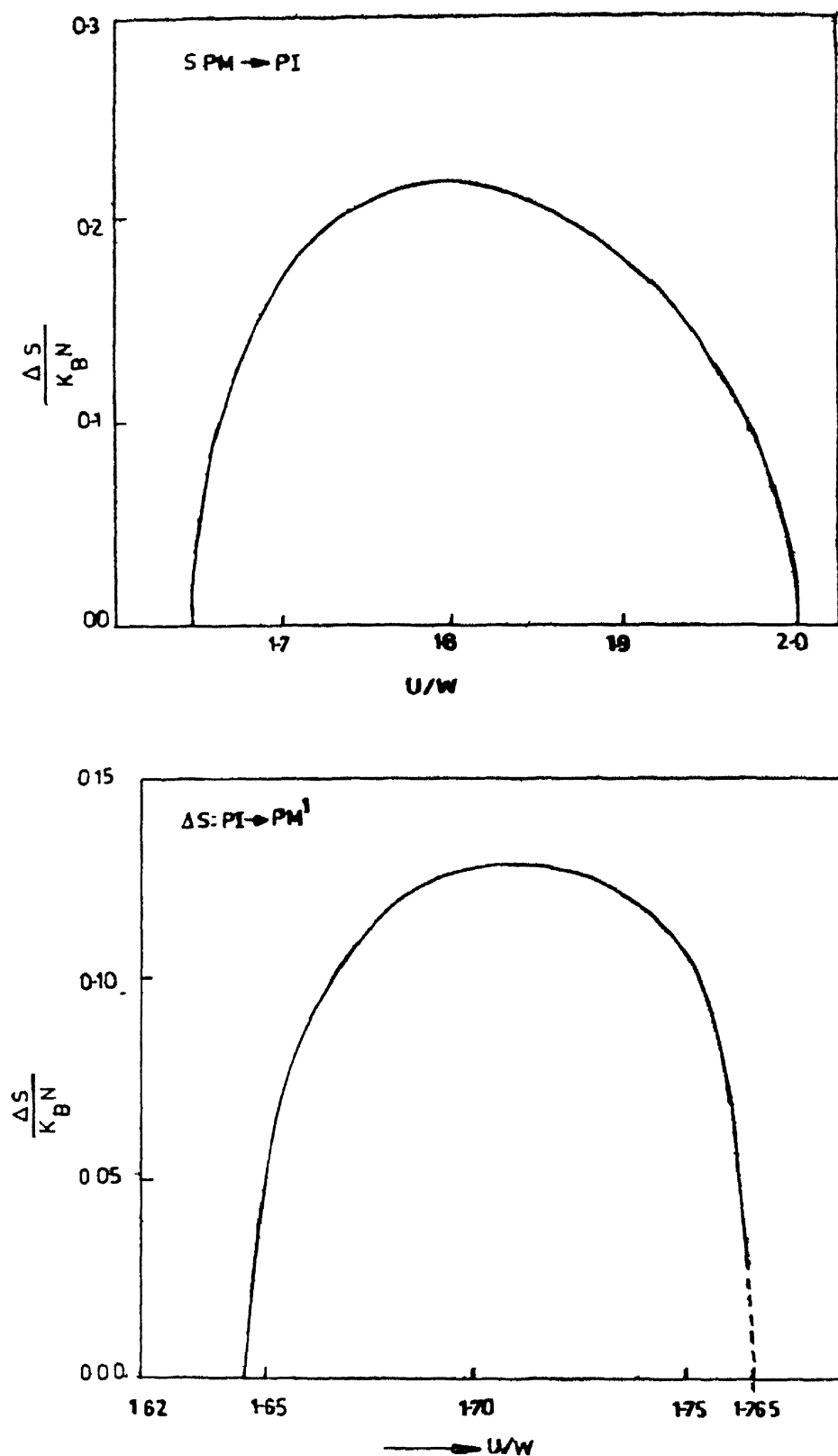


FIG 8 Plots of the reduced entropy discontinuity predicted at the first order phase transformations Part (a) PM-PI transition Part (b) PI-PM¹ transition Note that away from the critical U/W points the size of the entropy discontinuity peaks near the centre of the range in U/W where first order phase changes occur.

$$S_{Aj} \cdot S_{Bj'} \simeq \langle S_{Aj} \rangle S_{Bj'} + \langle S_{Bj'} \rangle S_{Aj} - \langle S_{Aj} \rangle \langle S_{Bj'} \rangle \quad \text{.. (29)}$$

$$v_{Aj} v_{Bj'} \simeq \langle v_{Aj} \rangle v_{Bj'} + \langle v_{Bj'} \rangle v_{Aj} - \langle v_{Aj} \rangle \langle v_{Bj'} \rangle \quad \text{.. (30)}$$

Let the magnetization be along the z -axis, then $S_{Aj} \cdot \langle S_{Bj'} \rangle = S_{Aj}^z \langle S_{Bj'}^z \rangle$ and $\langle S_{Aj}^z \rangle = -\langle S_{Bj'}^z \rangle = \langle S^z \rangle$. Also, $\langle v_{Aj} \rangle = \langle v_{Bj'} \rangle \equiv v$. On inserting these results into the last term of eq (28) and carrying out the indicated summations, we find

$$H_{ex} = -JZ \langle S^z \rangle \left[\sum_{j \in A} S_{Aj}^z - \sum_{\substack{j' \in B \\ j'(j)}} S_{Bj'}^z \right] + JZ \langle S^z \rangle^2 \frac{N}{2} - \frac{J}{4} Z \left\{ \sum_{j \in A} 2v v_{Aj} - \frac{N}{2} v^2 \right\} \quad \text{.. (31)}$$

Conservation laws [(eq 2) with $n = 1$] require that $v \equiv \langle v_{Aj} \rangle = 1 - 2\langle \eta_{Aj} \rangle \equiv 1 - 2\eta$. We also invoke the invariance requirement $\eta_{Aj} = \eta$, so that $v_{Aj} = 1 - 2\eta_{Aj} = 1 - 2\eta$, then eq (31) becomes

$$H_{ex} = -JZ \langle S^z \rangle \left[\sum_{j \in A} S_{Aj}^z - \sum_{\substack{j' \in B \\ j'(j)}} S_{Bj'}^z \right] + JZ \langle S^z \rangle^2 \frac{N}{2} - \frac{JZ}{8} N(1 - 2\eta)^2 \quad \text{.. (32)}$$

Next we introduce second quantization through the relations

$$S_j^z = \frac{1}{2} (n_{j\sigma} - n_{j-\sigma}) = \frac{1}{2} \sum_{\sigma} \sigma n_{j\sigma} \quad (\sigma = \pm 1), \quad \text{.. (33)}$$

wherein $n_{j\sigma}$ is the number operator with a value of 0 or 1 according as site j is not or is occupied by an electron of spin σ , the factor $\frac{1}{2}$ arises because in units of $\hbar$ the electron spin has the value $\pm \frac{1}{2}$. Then eq (32) becomes

$$H_{ex} = \frac{1}{2} JZ \langle S^z \rangle \left[\sum_{\substack{j' \in B \\ \sigma}} \sigma n_{Bj'\sigma} - \sum_{\substack{j \in A \\ \sigma}} \sigma n_{Aj\sigma} \right] + JZ \langle S^z \rangle^2 \frac{N}{2} - \frac{JZN}{8} (1 - 2\eta)^2 \quad \text{(34)}$$

At this point, it is expedient to introduce the Fourier transformation which converts creation and annihilation operators for direct space into corresponding quantities in reciprocal space

$$a_{Aj\sigma}^+ = \left(\frac{N}{2} \right)^{-1/2} \sum_{\mathbf{k}} a_{\mathbf{k}\sigma}^+ e^{i\mathbf{k} \cdot \mathbf{R}_j} \quad a_{Aj\sigma} = \left(\frac{N}{2} \right)^{-1/2} \sum_{\mathbf{k}} a_{\mathbf{k}\sigma} e^{-i\mathbf{k} \cdot \mathbf{R}_j} \quad \text{(35)}$$

By use of lattice sum rules it is then a straightforward exercise to show that $\sum_{j \in A} \sigma n_{Aj\sigma} = \sum_{\mathbf{k}} \sum_{\sigma} \sigma n_{A\mathbf{k}\sigma}$, whence,

$$H_{eq} = \frac{1}{2} JZ \langle S^z \rangle \left[\sum_{\mathbf{k}\sigma} \sigma (n_{B\mathbf{k}\sigma} - n_{A\mathbf{k}\sigma}) \right] + \frac{JZ \langle S^z \rangle^2 N}{2} - \frac{JZN}{8} (1 - 2\eta)^2 \quad (36)$$

We next turn our attention to the band energy term H_B in eq (28), however, to distinguish between itinerant electrons on A and B sublattices we must first transform back from reciprocal to real space, using transformations inverse to eq. (35) One can show without difficulty that this operation leads to

$$H_B \equiv \Phi \sum_{\mathbf{k}\sigma} \epsilon_{\mathbf{k}} a_{\mathbf{k}\sigma}^+ a_{\mathbf{k}\sigma} = \Phi \sum_{\sigma} \sum_{j'(j)} t_{jj'} a_{j'\sigma}^+ a_{j\sigma} \quad (37)$$

with

$$t_{jj} \equiv \left(\frac{N}{2}\right)^{-1} \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} e^{i\mathbf{k}(\mathbf{R}j - \mathbf{R}j')} \quad (38)$$

which permits one first to generalize eq (37) to a two-sublattice system

$$H_B = \Phi \sum_{\sigma} \sum_{j'(j)} t_{jj'} (a_{Aj'\sigma}^+ a_{Bj\sigma} + a_{Bj\sigma}^+ a_{Aj'\sigma}) \quad (39)$$

and then once more to switch back to reciprocal space via eqs (35) When the term so obtained is inserted for H_B , and after eq. (36) is used for H_{eq} , eq (28) reduces to the final form

$$H = \sum_{\mathbf{k}\sigma} \{ E_{\mathbf{k}} (a_{A\mathbf{k}\sigma}^+ a_{B\mathbf{k}\sigma} + a_{B\mathbf{k}\sigma}^+ a_{A\mathbf{k}\sigma}) + \sigma \Delta (n_{B\mathbf{k}\sigma} - n_{A\mathbf{k}\sigma}) \} + U\eta + JZ \langle S^z \rangle^2 \left(\frac{N}{2}\right) - JZN \frac{(1 - 2\eta)^2}{8} \equiv H_I + U\eta + H_M \quad (40)$$

with

$$\Delta \equiv \frac{JZ \langle S^z \rangle}{2} \text{ and } E_{\mathbf{k}} \equiv \Phi \epsilon_{\mathbf{k}} \quad (41)$$

Eq (40) must now be diagonalized. A very useful standard procedure in such a situation involves the so-called *Bogolyubov transformation* :

$$a_{A\mathbf{k}\sigma}^+ = u_{\mathbf{k}} \alpha_{1\mathbf{k}\sigma}^+ + v_{\mathbf{k}} \alpha_{2\mathbf{k}\sigma}^+ \quad (42)$$

$$a_{B\mathbf{k}\sigma}^+ = -v_{\mathbf{k}} \alpha_{1\mathbf{k}\sigma}^+ + u_{\mathbf{k}} \alpha_{2\mathbf{k}\sigma}^+ \quad (43)$$

in which $\alpha_{1\mathbf{k}\sigma}^+, \alpha_{2\mathbf{k}\sigma}^+$ replace the original operators $a_{A\mathbf{k}\sigma}^+, a_{B\mathbf{k}\sigma}^+$; the transformation set (42, 43) is unitary in that $u_{\mathbf{k}}^2 + v_{\mathbf{k}}^2 = 1$. It is a very straightforward but tedious procedure to substitute (42) and (43) for the operators in eq. (40) and to collect terms. After appropriate manipulations one obtains (we have suppressed some subscripts on α)

$$\begin{aligned} H_I = \sum_{\mathbf{k}\sigma} \{ & [-2E_{\mathbf{k}} u_{\mathbf{k}} v_{\mathbf{k}} - \sigma \Delta (u_{\mathbf{k}}^2 - v_{\mathbf{k}}^2)] \alpha_1^+ \alpha_1 + [2E_{\mathbf{k}} u_{\mathbf{k}} v_{\mathbf{k}} \\ & + \sigma \Delta (u_{\mathbf{k}}^2 - v_{\mathbf{k}}^2)] \alpha_2^+ \alpha_2 + (E_{\mathbf{k}} (u_{\mathbf{k}}^2 - v_{\mathbf{k}}^2) - 2\sigma u_{\mathbf{k}} v_{\mathbf{k}} \Delta) (\alpha_1^+ \alpha_2 \\ & + \alpha_2^+ \alpha_1) \} \end{aligned} \quad (44)$$

Without loss of generality one may require the multiplier of $(\alpha_1^+ \alpha_2 + \alpha_2^+ \alpha_1)$ to vanish which immediately diagonalizes H_I and thereby identifies the eigenvalues from the multipliers of $\alpha_1^+ \alpha_1$ and of $\alpha_2^+ \alpha_2$. For further ease of manipulation we set $u_{\mathbf{k}} \equiv \cos \theta_{\mathbf{k}}$, $v_{\mathbf{k}} \equiv \sin \theta_{\mathbf{k}}$, the vanishing of the multiplier in line 2 of eq. (44) together with $\cos^2(2\theta_{\mathbf{k}}) + \sin^2(2\theta_{\mathbf{k}}) = 1$, yields

$$\sin(2\theta_{\mathbf{k}}) = \pm \frac{E_{\mathbf{k}}}{[E_{\mathbf{k}}^2 + \Delta^2]^{1/2}} \quad \cos(2\theta_{\mathbf{k}}) = \pm \frac{\Delta}{[E_{\mathbf{k}}^2 + \Delta^2]^{1/2}}. \quad \dots(45)$$

The eigenvalues are now given by

$$E_{1\mathbf{k}} = -E_{2\mathbf{k}} = -2E_{\mathbf{k}} u_{\mathbf{k}} v_{\mathbf{k}} - \sigma(u_{\mathbf{k}}^2 - v_{\mathbf{k}}^2)\Delta = -[E_{\mathbf{k}}^2 + \Delta^2]^{1/2} \quad \dots(46)$$

in which we have kept as mutually consistent only the solution for which $\sigma = +1$.³⁶ As usual, the $N/2$ successive quantized $E_{\mathbf{k}}$ values are so closely spaced that they may be regarded as quasi-continuous. One should observe that the magnetic ordering phenomena cause a splitting of the band into two parts, $+ [E^2 + \Delta^2]^{1/2}$ and $- [E^2 + \Delta^2]^{1/2}$, with a gap of $2\Delta = JZ \langle S^z \rangle$, for large E the dispersion relation becomes nearly linear.

B Magnetization Effects

Our next task is to determine the net magnetization of the system in terms of the dimensionless parameter J/W . For this purpose we set up the expectation value $\langle S^z \rangle$ at zero temperature,

$$\langle S^z \rangle + \frac{1}{2} \frac{1}{N/2} \sum_{j \in A} (n_{A,j\sigma} - n_{A,j-\sigma}) \equiv \frac{1}{N} \sum_{\mathbf{k}\sigma} \sigma a_{A\mathbf{k}\sigma}^+ a_{A\mathbf{k}\sigma} \quad (47)$$

On introducing the Bogolyubov transformation we find

$$\langle S^z \rangle = \left(\frac{1}{N} \right) \sum_{\mathbf{k}\sigma} \sigma (u_{\mathbf{k}} \alpha_{1\mathbf{k}\sigma}^+ + v_{\mathbf{k}} \alpha_{2\mathbf{k}\sigma}^+) (u_{\mathbf{k}} \alpha_{1\mathbf{k}\sigma} + v_{\mathbf{k}} \alpha_{2\mathbf{k}\sigma})$$

$$= \left(\frac{1}{N} \right) \sum_{\mathbf{k}\sigma} \sigma [u_{\mathbf{k}}^2 \langle \alpha_{1\mathbf{k}\sigma}^+ \alpha_{1\mathbf{k}\sigma} \rangle + v_{\mathbf{k}}^2 \langle \alpha_{2\mathbf{k}\sigma}^+ \alpha_{2\mathbf{k}\sigma} \rangle] \quad (48)$$

in which the cross term in $\langle \alpha_1^+ \alpha_2 + \alpha_2^+ \alpha_1 \rangle$ was dropped since the Hamiltonian is already diagonalized. As before, we set $u_{\mathbf{k}} = \cos \theta_{\mathbf{k}}$, $v_{\mathbf{k}} = \sin \theta_{\mathbf{k}}$ and introduce eq (45) to obtain

$$\begin{aligned} \langle S^z \rangle = \frac{1}{N} \sum_{\mathbf{k}\sigma} \frac{1}{2} \sigma \left\{ \left[1 + \frac{\sigma \Delta}{(E_{\mathbf{k}}^2 + \Delta^2)^{1/2}} \right] \langle \alpha_{1\mathbf{k}\sigma}^+ \alpha_{1\mathbf{k}\sigma} \rangle \right. \\ \left. + \left[1 - \frac{\sigma \Delta}{(E_{\mathbf{k}}^2 + \Delta^2)^{1/2}} \right] \langle \alpha_{2\mathbf{k}\sigma}^+ \alpha_{2\mathbf{k}\sigma} \rangle \right\} \end{aligned} \quad (49)$$

On summing over σ , introducing $\Delta = (\frac{1}{2}) JZ \langle S^z \rangle$, and using Fermi-Dirac statistics (i.e. the Fermi-Dirac Function (51)) to replace expectation values of the operators we find

$$1 = \frac{1}{2} \frac{JZ}{N} \sum_{\mathbf{k}} \frac{f_{1\mathbf{k}} - f_{2\mathbf{k}}}{(E_{\mathbf{k}}^2 + \Delta^2)^{1/2}} \quad (50)$$

Now set $q_{\mathbf{k}} \equiv (E_{\mathbf{k}}^2 + \Delta^2)^{1/2} / k_B T$. Then the Fermi-Dirac Function becomes

$$f_{1,2\mathbf{k}} = f \left[\pm \frac{(E_{\mathbf{k}}^2 + \Delta^2)^{1/2}}{k_B T} \right] = \frac{1}{\exp(\pm q_{\mathbf{k}}) + 1} \quad (51)$$

so that eq (50) may be written as

$$\begin{aligned} 1 &= \frac{1}{2} \frac{JZ}{N} \sum_{\mathbf{k}} \frac{1}{(E_{\mathbf{k}}^2 + \Delta^2)^{1/2}} \left\{ \frac{1}{\exp(-q_{\mathbf{k}}) + 1} - \frac{1}{\exp(q_{\mathbf{k}}) + 1} \right\} \\ &= \frac{1}{2} \frac{JZ}{N} \sum_{\mathbf{k}} \frac{\tanh(q_{\mathbf{k}}/2)}{(E_{\mathbf{k}}^2 + \Delta^2)^{1/2}} \end{aligned} \quad (52)$$

Next, introduce the scaling law $E_{\mathbf{k}} = \Phi \epsilon_{\mathbf{k}}$ as before and change to an integration. As usual, the summation is replaced by $\left(\frac{N}{2} \right) \int d\epsilon \sum_{\mathbf{k}} \delta(\epsilon - \epsilon_{\mathbf{k}}) \rho_0^{\sigma}(\epsilon)$. This yields

$$1 = \frac{JZ}{4} \int_{-W/2}^{W/2} d\epsilon \rho_0^{\sigma}(\epsilon) \frac{\tanh(q_{\mathbf{k}}/2)}{[\epsilon_{\mathbf{k}}^2 \Phi^2 + \Delta^2]^{1/2}} \quad (53)$$

For the conventional rectangular DOS we find

$$1 = \frac{JZ}{2W\Phi} \int_0^{W\Phi/2} dE \frac{\tanh(q_{\mathbf{k}}/2)}{(E_{\mathbf{k}}^2 + \Delta^2)^{1/2}} \quad (54)$$

The integral may be evaluated for $\Phi \ll 1$ using Rolle's theory of the mean to obtain

$$1 = \frac{JZ}{4} \frac{\tanh \{[(W\Phi/4)^2 + \Delta^2]^{1/2}/2k_B T\}}{[(W\Phi/4)^2 + \Delta^2]^{1/2}} \quad (55)$$

and in the limit $\Phi \rightarrow 0$ and with $\Delta = JZ \langle S^z \rangle / 2$ this reduces to

$$\langle S^z \rangle = \frac{1}{2} \tanh \left[\frac{JZ \langle S^z \rangle}{4k_B T} \right] \quad (56)$$

C. The Ground State Energy

The ground state energy is specified by the expression

$$\begin{aligned} \frac{E_G}{N} = & \left(\frac{1}{N} \right) \sum_{\mathbf{k}\sigma} \{E_{1\mathbf{k}} \langle \alpha_{1\mathbf{k}\sigma}^+ \alpha_{1\mathbf{k}\sigma} \rangle + E_{2\mathbf{k}} \langle \alpha_{2\mathbf{k}\sigma}^+ \alpha_{2\mathbf{k}\sigma} \rangle\} \\ & - \left(\frac{JZ}{8} \right) (1 - 2\eta)^2 + U\eta + \frac{JZ \langle S^z \rangle^2}{2} \quad \dots(57) \end{aligned}$$

We now replace the two expectation values of the operators by $f_{1\mathbf{k}}, f_{2\mathbf{k}}$ as given by eq. (51) and we introduce (46). After considerable, through straightforward simplification the summation term yields

$$\frac{E_B}{N} = - \left(\frac{2}{N} \right) \sum_{\mathbf{k}} k_B T q_{\mathbf{k}} \tanh \left(\frac{q_{\mathbf{k}}}{2} \right) \quad (58)$$

We next switch to an integration to replace the summation, using the same procedure as in Sec IVB. We also introduce the conventional rectangular DOS. Then the summation term reads

$$\frac{E_B}{N} = - \left(\frac{2}{W} \right) \int_0^{W/2} d\epsilon [(\Phi \epsilon_{\mathbf{k}})^2 + \Delta^2]^{1/2} \tanh \left\{ \frac{[(\Phi \epsilon_{\mathbf{k}})^2 + \Delta^2]^{1/2}}{2k_B T} \right\} \quad (59)$$

For $\Phi \ll 1$, the integral may be evaluated by using Rolle's theorem, which leads to

$$\frac{E_B}{N} = - \left[\left(\frac{\Phi W}{4} \right)^2 + \Delta^2 \right]^{1/2} \tanh \left\{ \frac{[(\Phi W/4)^2 + \Delta^2]^{1/2}}{2k_B T} \right\} \quad (60)$$

and as $\Phi \rightarrow 0$ this simplifies to

$$\frac{E_B}{N} = - \left(\frac{JZ \langle S^z \rangle}{2} \right) \tanh \left(\frac{JZ \langle S^z \rangle}{4k_B T} \right) \quad (61)$$

Finally, introducing eq (56) one finds the simple expression

$$\frac{E_B}{N} = - JZ \langle S^z \rangle^2 \simeq - \frac{JZ}{4}, \quad (62)$$

where the term on the right is a limiting case at low temperature in the mean field approximation $\langle S^z \rangle = \frac{1}{2}$ (in units of $\hbar$). The ground state energy in this approximation is found from eq (57) to be

$$\frac{E_G}{N} = -\frac{JZ}{4}, \quad (63)$$

where we have set $\eta = 0$, consistent with the earlier approximation of taking $\Phi = 0$

D The AFI-PM Transition

At this stage we can inquire under what circumstances a transition from the antiferromagnetic insulating state to the correlated metallic state can take place. The necessary and sufficient condition is that $(F/N)_{\text{AFI}} = (F/N)_{\text{PM}}$. For the AFI phase we use a drastic simplifying assumption; namely, we equate F/N with E_G/N , as given by eq. (63); for, as is well established, the entropy contributions to the free energy of the magnetically ordered insulator are small in the low temperature range for which the derivation leading to (63) is valid. Furthermore, we neglect any changes in W arising from magnetic ordering effects. Eq (11) specifies the chemical potential for the correlated metal. On (i) equating these relations, (ii) introducing the expression $\Phi = 1 - (U/2W)^2$, and (iii) the formulation $\eta = (1/4)(1 - U/2W)$, both valid at low temperatures for the PM phase, one can solve for

$$\frac{k_B T}{W} = \left\{ \frac{3\Phi}{\pi} \left[\frac{JZ}{4W} - \frac{1}{4} \left(1 - \frac{U}{2W} \right)^2 \right] \right\}^{1/2} \quad (64)$$

which represents the equation for the reduced antiferromagnetic transition temperature in its dependence on the U/W parameter. This relation with $J = 4t^2(1 - \Phi)/U$ and $t = W/2Z$, $Z = 4$ is sketched as the lower left curve for the phase diagram, Fig. 9.

E The AFI-PI Transition

An analysis comparable to that of the preceding Section may now be carried out to establish the phase boundary separating the AFI and PI phases. For this purpose we equate E_G/N , eq. (63), with F_{PI}/N as read off from eq (13). Once again, one must bear in mind the many approximations that are invoked to arrive at these limiting expressions. The final result is specified by

$$\frac{k_B T}{W} = \frac{JZ}{4} \ln 2 \quad (65)$$

with $J = 4t^2(1 - \Phi)/U$ and $t = W/2Z$, $Z = 4$ as before. A plot of $k_B T/W$ vs. U/W resulting from the above is shown as the lower right curve in Fig. 9.

VI DISCUSSION

The final theoretical phase diagram is exhibited in Fig. 9 for the theory developed in Secs VD and VE. One should first recall again the many restrictions and

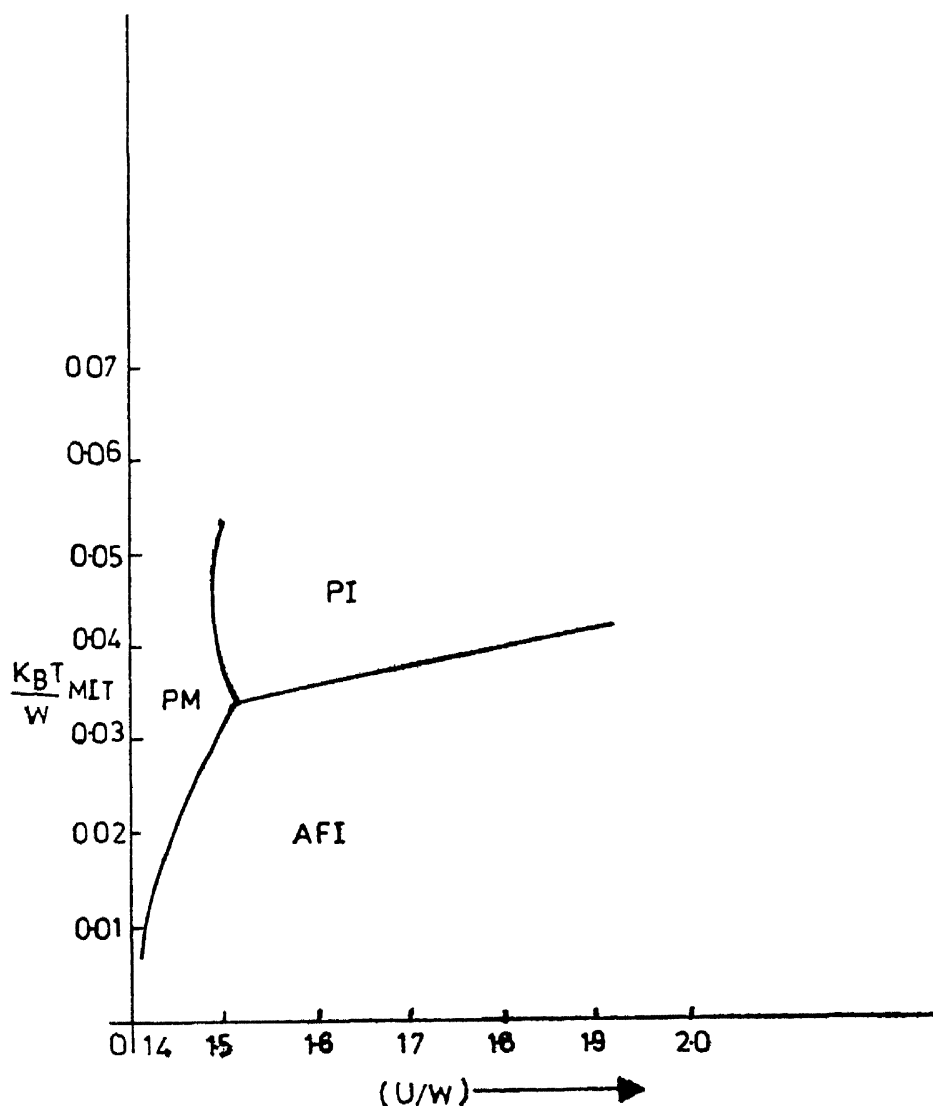


FIG 9 Final form of the theoretical phase diagram in the low temperature approximation as developed in Sec VD and VE. Note the triple point. For the higher-temperature paramagnetic regime in excess of $(k_B T / W)_t$ the more exact theory leading to the results of Fig. 7 must be used.

assumptions that led to this formulation. The theory is based on the existence of a nondegenerate band that is exactly half-filled, a single scaling function Φ was used to relate the energies E_k and ϵ_k of the quasiparticles and of the bare particles, electron interactions are simulated by the single parameter U , a rectangular DOS was invoked to evaluate the integrals specifying band energies in the PM and PI phases, the low temperature limiting form was invoked and, in particular, the energy of the AFI phase was used as an approximation to the actual free energy of the magnetically ordered insulator.

One should clearly recognize that the results leading to Fig 9 really only apply in the limit $T \rightarrow 0$, and already differ significantly from the more sophisticated theory of Sec. IV in which the limiting case $T \rightarrow 0$ is not invoked. Unfortunately,

at the time of writing, the corresponding more sophisticated theoretical calculations pertaining to the AFI $\rightarrow$ PM and AFI $\rightarrow$ PI transitions were not yet available. Thus, the phase diagram of Fig. 9 is to be regarded as an approximation to the results anticipated for the improved theories that are not based on the limit $T \rightarrow 0$. Subject to these limitations one encounters a triple point at $k_B T/W \simeq 0.034$, $U/W \simeq 1.515$ for the coexistence of the AFI, PM and PI phase. The phase boundaries for the paramagnetic regime at reduced temperatures in excess of 0.034 are to be read off from Fig. 7, based on the improved theory of Sec. IVD.

Despite all of the simplifications that have been introduced at various stages the theory does provide a relatively good account of the properties of the $(V_{1-x}\text{Cr}_x)_2\text{O}_3$ alloy system. In particular, it is evident that all the cases discussed in Sec. I have their theoretical counterpart in the phase diagrams of Fig. 7 and Fig. 9; depending on the value of U/W which a adopted one may encounter zero, one, two, or three transitions when the temperature is altered. Only so long as U/W remains above a critical value (which is temperature-dependent and which approaches $(U/W)_{\text{cr}} = 2$ as $T \rightarrow 0$ for a rectangular DOS) does one deal with a case where itinerant electrons are absent from the system, such a solid is a Mott-type insulator in the sense originally proposed by Mott.¹⁶

To permit a comparison to be made between the theoretical and experimental phase diagrams we now establish that U/W varies nearly linearly with the mole fraction x of Cr. To do so we adopt the virtual crystal approximation in which the Hubbard parameter U is replaced by an effective parameter U_e specified by

$$U_e = U_v(1 - x) + U_{\text{Cr}}x \quad (66)$$

A corresponding effective bandwidth, W is also required. For this purpose one may adopt the proportionality $W \sim t_{ij} \sim \exp(-\lambda R_{ij})$ involving W and the transfer integral t_{ij} between nearest neighbors i and j separated by the distance R_{ij} ; λ is a scaling factor. The various transitions of the V_2O_3 system are accompanied by sizeable volume changes Δv in the unit cell volume v_0 . We then write $t_{ij} \simeq \exp[R_{ij}^0 + A\Delta R_{ij}] = \exp\{-[R_{ij}^0 + Bx(\Delta v/v_0)^{1/3}]\}$, wherein R_{ij}^0 is a reference interatomic separation, and $A\Delta R_{ij}$ is the change in separation introduced by replacing a vanadium atom in location j by Cr. In accord with Vegard's law, for dilute concentrations one may anticipate that $A = Bx$ is proportional to the mole fraction of the diluent. On expanding to first order terms one obtains

$$t_{ij} \sim \{\exp(-\lambda R_{ij}^0) \left[1 + Bx \left(\frac{\Delta v}{v_0} \right)^{1/3} \right]\}, \quad (67)$$

whence

$$W_e = W \left[1 + Bx \left(\frac{\Delta v}{v_0} \right)^{1/3} \right] \equiv W_v + (W_{\text{Cr}} - W_v)x \quad (68)$$

Finally, then,

$$\left(\frac{U}{W} \right)_e = \frac{U_v + (U_{\text{Cr}} - U_v)x}{W_v + (W_{\text{Cr}} - W_v)x} = \frac{U_v}{W_v} \left[1 + \frac{U_{\text{Cr}} - U_v}{U_v} + \frac{W_v - W_{\text{Cr}}}{W_v} x \right] \quad (69)$$

which shows explicitly the linear variation of U/W with x in the present approximation

U/W may further be altered by the atomic potential fluctuations that arise when Cr is substituted for V. Let $\Delta\epsilon \equiv \epsilon_{Cr} - \epsilon_v < 0$ be the energy difference for an electron localized at a Cr as compared to a V atom. The expectation value of the energy is then given by $\sum_{(i,\sigma)} E_i \langle n_{i,\sigma} \rangle$, where E_i may assume the values E_{Cr} or E_v depending on the site index i . This expectation value may be simulated by the product $(1 - \Phi) x \Delta\epsilon$. The first factor pertains to the probability that an electron is actually localized (See Sec. IVA), the factor x represents the probability that a site containing a Cr atom is encountered. The inhomogeneity arising from the Cr substitution thus enhances localization as expressed through the factor $(1 - \Phi)$; this correction must be added to the energy contribution $-(W/U)\Phi$ as specified in eq. (6); we obtain an effective band energy

$$\frac{E_B}{N} = x\Delta\epsilon - \left(\frac{W}{U}\right) \left[1 + \left(\frac{4\Delta\epsilon}{W}\right) x \right] \Phi. \quad (70)$$

Since $\Delta\epsilon < 0$, the multiplier $[1 + (4\Delta\epsilon/W)x]$ represents an additional band narrowing factor associated with the lattice disorder due to the random distribution of Cr atoms. This factor is a linearized form of the Anderson localization effect arising from the presence of randomly fluctuating potentials in the lattice.

The total variation of (U/W) with x is then given by the linear relationship

$$\frac{U}{W} = \frac{U_v}{W_v} \left[1 + \left(\frac{U_{Cr} - U_v}{U_v} \right) + \left(\frac{W_v - W_{Cr}}{W_v} - \frac{4\Delta\epsilon}{W_v} \right) x \right] \quad \dots(71)$$

The above permits $k_B T/W$ and U/W to be replaced with $k_B T/W_v$ and $(U/W)_v$ respectively and to be linearized as shown in eqs. (68) and (71).

One should not set too much store by the numerical values assigned to the critical points identified in Fig. 7 or 9 or to any other values which might be obtained by a fit to experimental data. These fits are all derived for the special case $n = 1$ and are sensitive to the type of DOS employed in the evaluation of the integrals specifying the band energies. The main point is that a consideration of electron correlation effects alone already provides a mechanism for a basic understanding of the set of phase transitions as well as of the reentrant metallic properties in the $(V_{1-x}Cr_x)_2O_3$ system. However, there are two important qualifications that must be carefully kept in mind.

First, the numerical predictions are somewhat off the mark. For example, the calculated entropy changes shown in Fig. 8 are too high by a factor of two relative to the experimental values cited by the Purdue group^{37a}. Also, the $PI \rightarrow PM'$ transition which is predicted to be of first order is actually spread out over a very large temperature range, if one attempts to circumvent this problem by choosing a U/W just slightly larger than the value corresponding to the upper terminal point in Fig. 7 then one does obtain a continuous $PI \rightarrow PM'$ transition as shown in Fig. 6(b). However, the predicted low-temperature $PM \rightarrow PI$ transformation is too large by many orders of magnitude. Lastly, the predicted transition temperatures read off

from Fig 7 and 9 are too high by a factor of two or three, unless one chooses unrealistically small values $W \leq 0.3\text{eV}$ for the bare-particle band-width

Second, there is unmistakable experimental evidence to the effect that the lattice plays an important role in the transition. This is brought out clearly in several types of experimental measurements —

X-ray diffraction experiments^{7,38} indicate that there is a sizeable expansion of the lattice during the PM $\rightarrow$ AFI and PM $\rightarrow$ PI transitions.

(ii) Raman scattering experiments^{39–41} show that virtually all Raman-active modes alter in frequency during the transitions.

(iii) There are enormous hysteresis effects of ca. 50 K¹⁴ in the PM $\rightarrow$ PI transition, and for magnetic ordering transitions that occur below 50 K.

(iv) Ultrasonic measurements^{42–44} show that certain elastic constants of the alloys soften near the AFI-PI or AFI-PM phase changes.

(v) Careful X-ray studies have revealed the existence of Bragg satellite spots⁴⁵ that have been interpreted as indicating the onset of charge-density waves coincident with the PM $\rightarrow$ PI transition

(vi) Inelastic neutron scattering experiments^{46,47} have shown that low frequency longitudinal optical lattice vibrational modes are encountered in the alloy system along certain directions in reciprocal space.

The data are shown in Fig. 10, one should note the anomalies in the lower lying acoustic phonon branches. The interpretation of the splittings and the

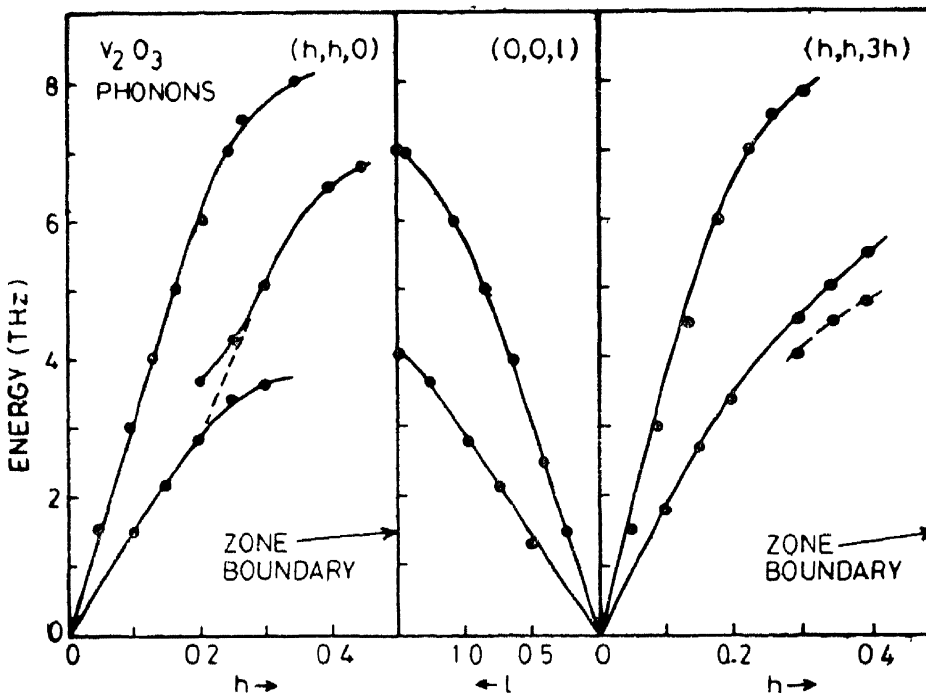


FIG 10 Acoustic phonon branch spectrum at 300 K for V_2O_3 as determined from inelastic neutron scattering experiments. Note the anomalous lower-lying branches

presence of what may be low-lying optical modes is unclear at this point, but they are presumably correlated with peculiarities in the lattice dynamics of V_2O_3 .

The above features indicate that the lattice is not passive in the initiation of phase changes in the V_2O_3 alloy system. Thus, a more complete theory would require the inclusion of the energy and entropy of the lattice in the construction of the total free energy before the latter is minimized. Attempts to do so are currently in progress.

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DIVIDED METALS

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In this lecture, I intend to present a very brief overview of the question of the electronic structure of metals which are neither quite macroscopic, nor microscopic in nature. Our interest in these Divided Metals is motivated by the need to understand the metallic and nonmetallic states of matter, for it can be asserted that to understand either regime one must elucidate the manner in which bulk, macroscopic states of matter evolve from the progressive agglomeration of atomic constituents. Alternatively, Divided Metals can be viewed as arising from the bulk metallic phase *via* subdivision of a macroscopic solid.

The questions to raise, therefore, are both experimental and theoretical. How does one connect the microscopic world of atomic and molecular clusters with the macroscopic world of metals and insulators? In what manner can one probe experimentally the progressive evolution of bulk properties, as a function of number or size? and how does one begin to formulate a conceptual picture of this evolution? The present work, then, attempts to touch upon two such interwoven themes: metal-insulator transitions and the evolution of macroscopic states of matter from progressive agglomeration of their atomic siblings. The title of this talk originates from Faraday's work on gold in a metallic, divided state, published over a century ago.

INTRODUCTION

In 1857, Michael Faraday presented his Bakerian Lecture entitled¹ "Experimental Relations of Gold (and Other Metals) to Light". Faraday's work on gold, silver and other metals led him to conclude that "*.. the gold is reduced in exceedingly fine particles which becoming diffused, produce a beautiful fluid. the various preparations of gold whether ruby, green, violet or blue consist of that substance in a metallic divided state*"². A present day investigation² of metallic, divided gold—colloidal gold—can reveal just how close to the truth were Faraday's conceptions of the problem some 130 years ago. Fig 1 (a) shows electron microscope photographs of submicron-sized colloidal gold particles prepared from the reduction of chlorauric acid with sodium citrate. In Fig 1 (b) is shown a high resolution electron microscope picture of an individual gold particle in which one begins to see the detailed structure of the metal particle at the nanometer level.

²²Characters in bold face added by the author

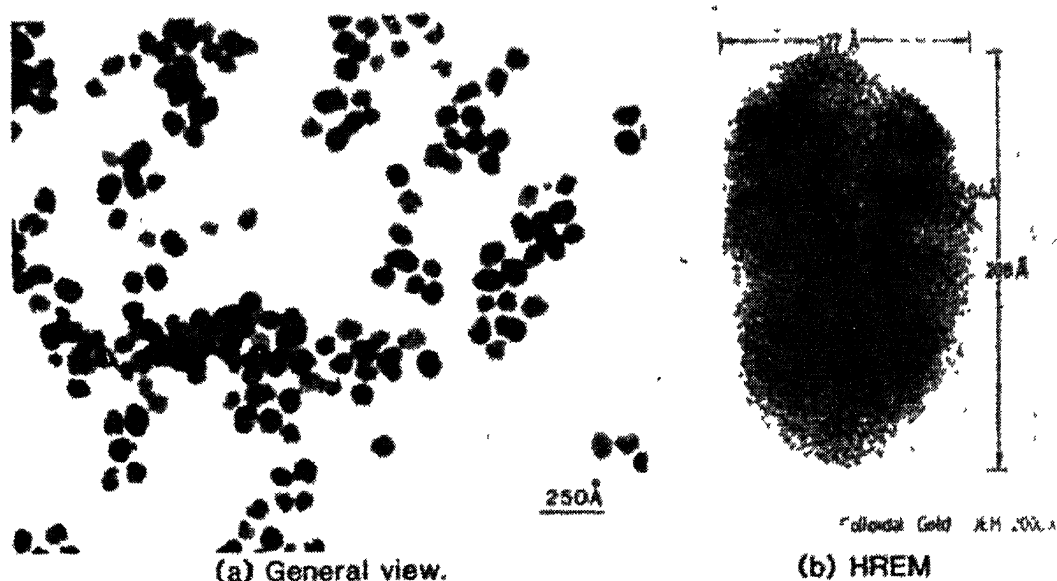


FIG 1 Colloidal gold particles prepared from a chlorauric acid solution reduced with sodium citrate. A High Resolution Electron Microscope picture of an individual gold particle is also shown.^{21,26}

In the present work, an attempt is made to review certain aspects of the current state of investigations—both theoretical and experimental—of the electronic structure of metal particles which are neither quite microscopic nor macroscopic in nature. This short paper cannot hope to go into the details of the very rich and diverse properties of divided metals, rather, it will concentrate only on giving a representative outline of a variety of observations on divided-metal systems ranging from transition metal cluster compounds to colloidal metals. Throughout the bias will be towards studies carried out in the author's own laboratory.

An artist's impression of the problem at hand is given in Fig 2, this sets out the broad, global features while at the same time it attempts to provide a rough labelling or classification scheme for particles of different dimensions. These range from bulk, metallic solids through colloidal metals to metal cluster compounds (typically of the transition series). Clearly at each stage along the way (Fig 2), one has to consider not only the macroscopic topology of such divided or erstwhile metals, but also their microscopic structure, *vis-a-vis*, the detailed nanostructure of the individual atomic constituents. Thus, particle diameters probably represent a reasonable coarse-grained parameter for arbitrarily classifying the various categories. In the case of the "atomic or molecular" transition metal cluster compounds³ (e.g. $\text{H}_2\text{Os}_{10}\text{C}(\text{Co})_{24}$), the cluster nuclearity is perhaps a more meaningful descriptive parameter which is certainly consistent with the atomic parentage of these species. We see, for example, in the cluster compound⁴ $\text{Au}_{55}[\text{P}(\text{C}_6\text{H}_5)_3]_{12}\text{Cl}_6$ a gold cluster of an exceptional size for a molecular species. However, by the standards of colloidal gold science—in which one is typically dealing with Ca.

DIVIDED METALS

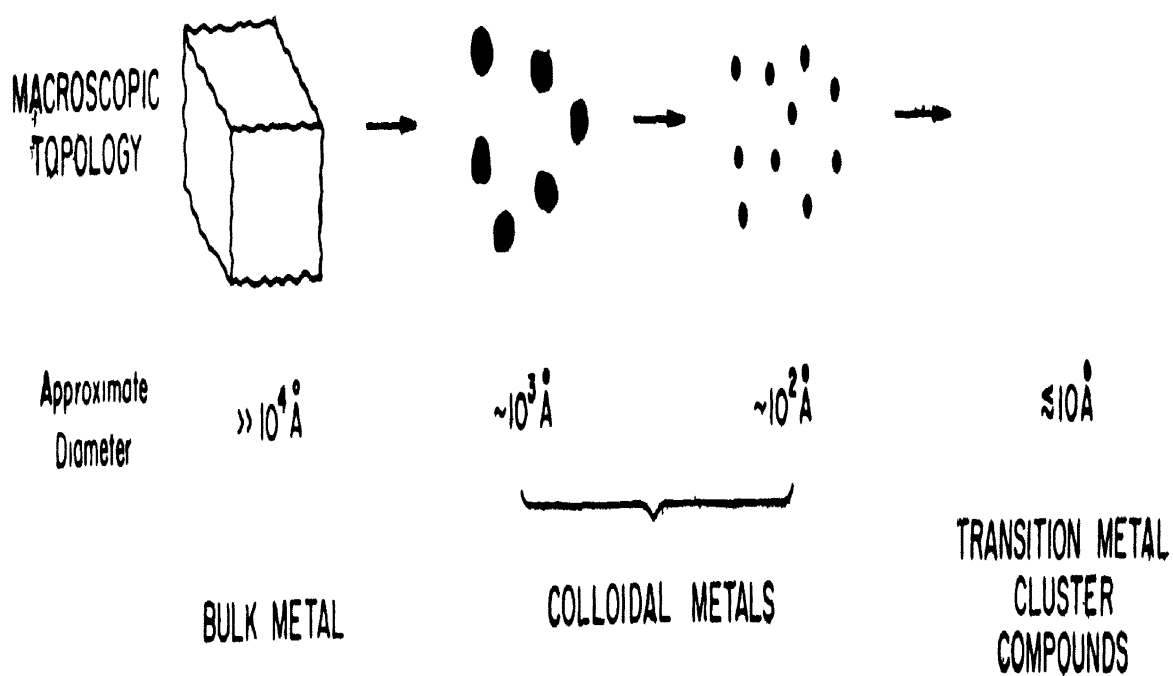


FIG 2 An artist's impression of the fragmentation or division of a bulk, metallic sample

10^3 – 10^6 atoms in a fragment—such a particle is extremely small. But these are vexing questions of semantics which must necessarily arise in any discussion of materials which effectively provide the link between the macroscopic and microscopic regimes of matter

One imagines that there must surely be a fundamental and qualitative difference between a piece of bulk, metallic gold and a relatively small collection of gold atoms (for example, in a colloidal particle) despite the fact that both consist of the same element. Our major problem, then, is the combined one of the synthesis of high-purity materials and the measurement of physical properties which reflect the successive fragmentation, or division, of a piece of bulk metal. Experimental techniques must yield formation on macroscopic morphology while at the same time probe both the nanostructure and electronic structure of Divided Metals

ELECTRONS IN DIVIDED METALS

In a recent elegant contribution, Perenboom, Wyder and Meier⁵ outline the broad feature of the problem of Divided Metals, “When the number of atoms contained in a grain of solid matter is steadily reduced, it is plausible that in the course of the process a stage is realized when the particle does not behave like a smaller copy of the corresponding bulk solid anymore.” The last part of this statement . .

“ . when the particle does not behave like a smaller copy of the corresponding bulk solid anymore,”

beautifully typifies the basic experimental and theoretical interest. I suggest, therefore, that two fundamental theoretical aspects need to be addressed⁶. The first concerns the possible electronic transition from metallic to insulating behaviour *within each grain* of solid matter. The second concerns the electronic and structural properties of small, isolated, but almost certainly “metallic,” particles

Localization, Charge Neutrality and the Metal-Insulator Transition

One inevitable consequence of the successive fragmentation of a piece of metal is the cessation of conducting behaviour within a small particle. A stringent lower limit for this transition would obviously be a cluster of only a few atoms. However, one clearly wishes to probe this Metal-to-Insulator Transition in more searching detail. Is there, for example, any similarity between the well-documented and prescribed descriptions for the Metal-Insulator Transition in what one might term “conventional” macroscopic systems (e.g. doped semiconductors)⁷ and the proposed transition within a single particle in isolation? A schematic illustration of the possible situation in doped semiconductors and Divided Metals is given in Fig. 3. It is interesting to note that Sir Nevill Mott, in his celebrated paper⁸ of 1961 entitled “The Transition to the Metallic State” alluded to just such a discussion. Concerning the proposed first order (discontinuous) nature of the transition in macroscopic systems, Mott noted⁸ that “*the sharp transition described here is only expected in an infinite lattice. It goes without saying that for a finite number of atoms there will be a gradual decrease in the weight of the ionized states in the wave*

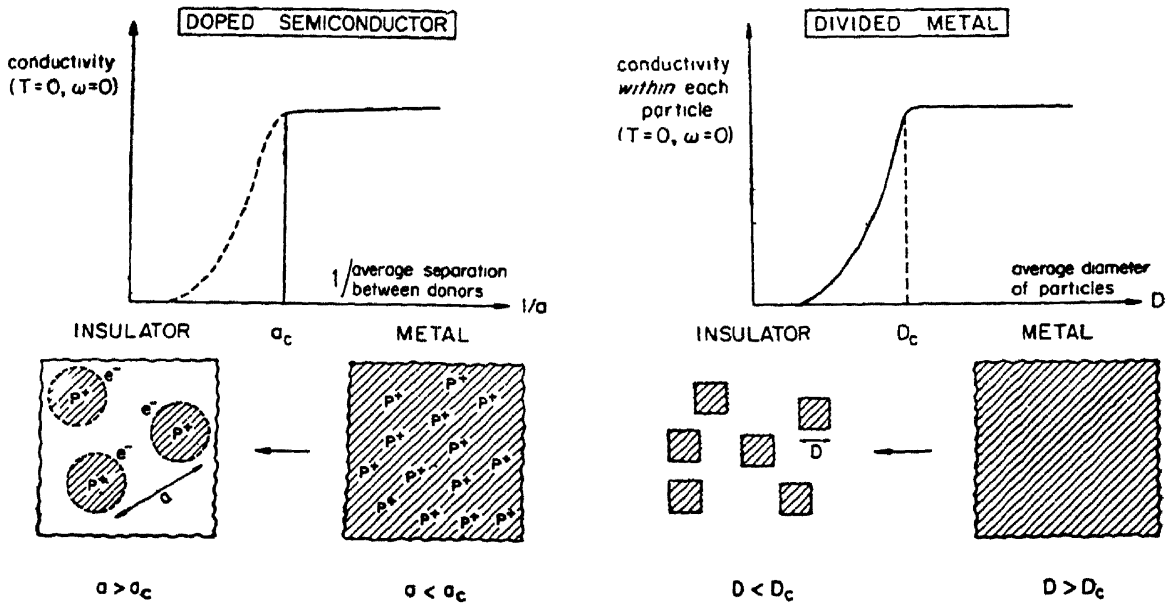


FIG 3 The Metal-Insulator transition in doped semiconductors and divided metals. A schematic representation which attempts to highlight the similarities and possible differences between the two situations at $\omega = 0$, $T = 0$ K.

function as the interatomic distance is increased or in other words, a gradual transition." Fig. 3 attempts to illustrate the two situations. In the case of doped semiconductors, the transition from Metal to Insulator is effected by varying the donor (P^0) atom concentration. Thus, the average separation (a) between donor states provides the demarcation between metallic ($a < a_c$, where a_c is the critical separation) and insulating ($a > a_c$) states in an (assumed) macroscopic assembly. The corresponding proposed transition within a Divided Metal would arise from a diminution in the average diameter (D) of the individual particles. Here, the critical parameter may now be D , such that $D > D_c$ implies metallic status (for $\omega = 0$, $T = 0$), whereas $D < D_c$ implies insulating character. However, it may turn out that more detailed views of such a transition, involving a scaling theory for electrons in a disordered small particle, may also lead to a continuous conductivity transition in both representative systems.⁹

Wood and Ashcroft¹⁰ make another interesting comparison between the two situations (Fig. 3). The Ioffe-Regel¹¹ criterion for the localization of electrons in the presence of scattering $1/\tau$, the breakdown of the Boltzmann equation approach to conduction in a solid, is

$$k_F l \lesssim 2\pi, \quad (1)$$

where l is the electron mean-free path and k_F is the Fermi wave-vector appropriate to the electron density. Thus, Ioffe and Regel¹¹ argued that since l is the distance over which the electron loses phase coherence, and the wavelength ($\lambda \sim k_F^{-1}$) is the distance over which the phase changes by 2π , it does not make sense to $\lambda \gg l$.

Wood and Ashcroft¹⁰ suggest that if one crudely interprets l as a characteristic small-particle dimension (say, the diameter D), then the cessation of conducting behaviour in a small particle may be interpreted as a Metal-Insulator Transition of the Ioffe-Regel sort. For sodium metal, this transition should occur for particle dimensions below approximately $15\text{\AA}$.

In all of these considerations, however, the immediate and fundamental problem arises as to the "true" dimensions of a small particle. Here a knowledge of structural details at the nanometer level is essential (Fig 1). That is, the particle itself may well be a collection of compact, finite sized metal-cluster subcomposites. For example, a particle of outside dimensions of say $1000\text{\AA}$ may consist of isolated metal-particle clusters with characteristic radii $100\text{\AA}$! It may also be the case—especially if these regions are not in close contact—that the electron mean free path (and corresponding scattering times, etc.) is dominated by the single particle dimension rather than the much larger particle dimension. This feature, noted recently by Curtin and Ashcroft,¹² will be discussed further in Sec. III 4.

In discussing the interparticle interactions within these divided metals, another interesting analogy can be made with the Metal-Insulator Transition in nominally macroscopic systems (Fig 4). It is generally assumed that the electron number in each small metallic particle is constant. This innovation, due originally to Kubo¹³

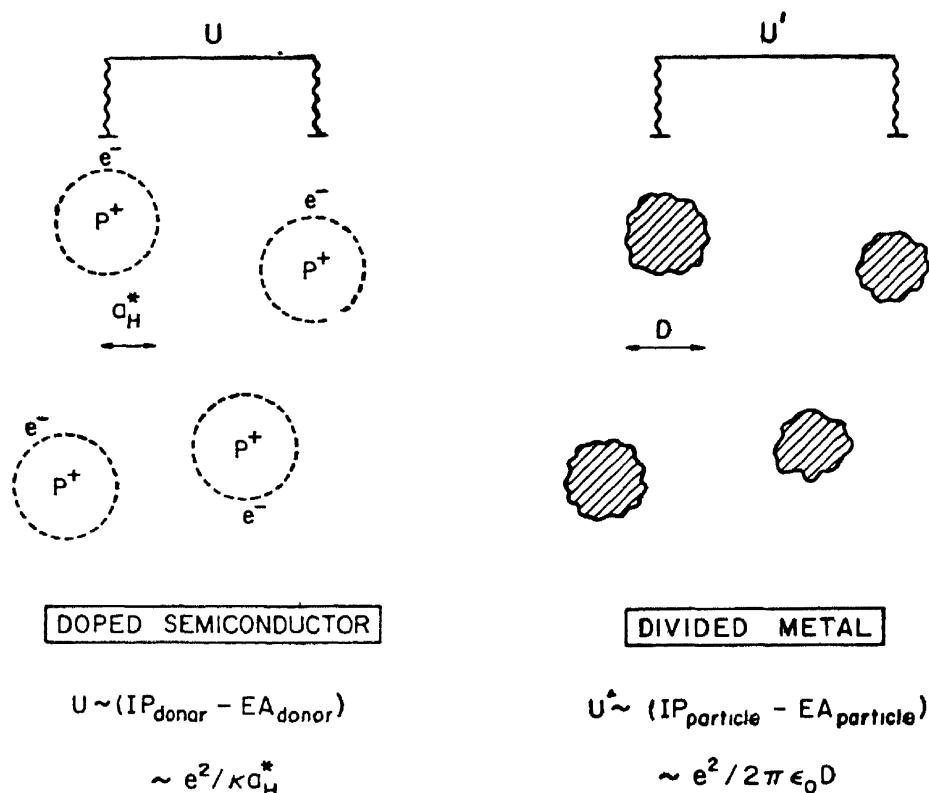


FIG 4 The metal-insulator transition in doped semiconductors and divided metals. A schematic representation of the Mott-Hubbard Correlation Energy, U , in the doped semiconductor, and the corresponding U' "charging energy" which maintains electrical neutrality in the Divided Metal.

has its "atomic" counterpart in the Mott-Hubbard correlation energy, U . The energy required to charge a metallic particle of diameter D with a charge in a vacuum is $U' \approx e^2/2\pi\epsilon_0 D$, where ϵ_0 is the vacuum permittivity. This charge can only originate from the surrounding medium which is at a temperature T . Therefore, when kT ($\sim 10^{-4}$ eV at 1 K, ~ 0.03 eV at 300K) is less than $e^2/2\pi\epsilon_0 D$ (~ 0.2 eV for $D = 100\text{\AA}$), the probability of electron transfer between particles is very small and therefore charge fluctuations are highly improbable. Note however, that such considerations tell us little about electron-electron correlation effects *within* a metal particle. One might imagine that for large metallic particles—in particular those in reasonable proximity to adjacent particles—this charging energy is small such that charge fluctuation may indeed occur. This situation is somewhat analogous to that found, for example, in doped semi-conductors and expanded metals *vis-à-vis*, the Mott-Hubbard correlation induced Metal-Insulator Transition.⁹ The Mott-Hubbard correlation term U is, in the atomic limit, the difference between the ionization energy (IP_{donor}) of the donor and the electron affinity of the donor (EA_{donor}) and $U \sim e^2/\kappa a_H^*$, where κ is an appropriate dielectric constant and a_H^* is the characteristic Bohr-orbit radius of the isolated donor state (Fig. 4).

Small Metallic Particles

A reasonable working definition might be a small particle which possesses a considerable and sufficient number of electrons such that the usual descriptions and methodology of solid state (metal) physics remain appropriate. Thus, one approach to the problem depicted in Fig. 2 revolves around the consequences of particle fragmentation within the framework of what one might term "bulk" solid state theory. Obviously, modifications due to the "smallness" of the system are added as a sort of perturbation. This approach would, presumably, be inappropriate for metal cluster compounds consisting of, say, 10 metal atoms, which one might deem to be approaching the atomic or molecular limit. However, as pointed out elsewhere,^{5,6} it should give most useful and intuitive information when the particle dimensions are such that a realistic description is indeed one in terms of gradually reducing the size of the macroscopic, solid sample. In this spirit, a small metallic particle can then be considered as a solid with dimensions comparable to, or smaller than, some intrinsic length, for example, the electron mean-free path, the wavelength of light, etc.

It is important to reiterate the view^{5,6} that a very clear distinction has to be made between the electronic energy-level structure of the full thermodynamic, many-particle system, and the electronic structure of a *single* quantum-mechanical particle, both in a finite volume.

In a bulk metal, the electron energy levels form a continuous set which are generally interpreted as being independent of any particular boundary conditions imposed on the electron wave-function. This standard picture must clearly be modified for metallic particles of dimensions smaller than, say, $10^3\text{\AA}$. Thus, the imposed truncation of the one-electron wave-function has two effects on the electronic properties of the particle.⁵ The first is a surface effect. The fraction of surface atoms

increases rapidly as the particle diameter decreases. For example, Fig 5 shows the effective fraction of surface atoms for sodium particles of various diameters. Thus, for sodium particles of less than 100 Å diameter, at least 10 per cent of the constituent atoms are located on the particle surface

The second effect results from the imposed discreteness of the electronic energy levels due to the smallness of the system. For a particle containing N atoms, the spacing (Δ) of adjacent energy levels will be of the order* of E_F/N , where E_F is the Fermi energy appropriate to the bulk metal. It is perhaps obvious (especially in hindsight), as was realized many years ago, that interesting effects should occur if the average value of Δ for a particle becomes comparable to, or greater than, some important characteristic energy. For example, when Δ is larger than the thermal energy, kT , the electronic Zeeman energy ($g\mu_B H$), the energy of incident radiation ($\hbar\omega$) etc.

The resulting consequences are generally termed quantum-size effects. In Fig. 5, we also show the average one-electron energy level gap (calculated for

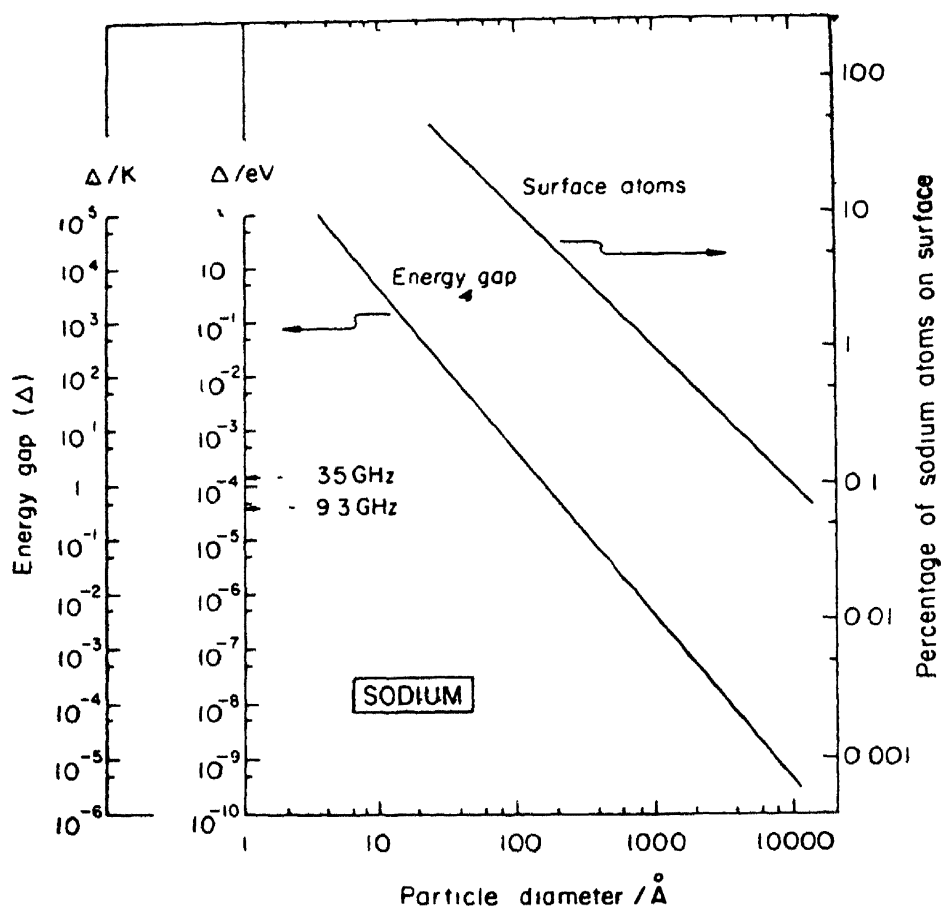


FIG 5 The fragmentation of bulk sodium metal. A plot of the average energy level separation as a function of the particle diameter D . The figure also shows the calculated surface fraction of atoms in a particle as a function of particle diameter.

*See also ref. 10 for a discussion of this point

sodium using $\Delta \sim E_F/N$) as a function of particle diameter, with Δ parameterized in both eV and K. Therefore, one anticipates size effects to be important, for example, when $\Delta \gtrsim kT$, so that for a Na particle with $D \sim 100\text{\AA}$, this condition would be satisfied below approx. 5 K, for a particle with $D \sim 30\text{\AA}$ the corresponding temperature is 300 K. We also indicate in Fig. 5, the typical values of the electron spin Zeeman energies at both X- and Q-band operating frequencies. It seems clear, therefore, that for particles with diameters below ca. 200–300 Å, magnetic susceptibility, magnetic resonance and many other properties (e.g. optical) may be greatly affected by this energy level structure. In addition, it is widely supposed^{13,14} that the dynamic response of both electrons and nuclei in small metallic particles at a frequency ω such that $\Delta \gtrsim \hbar\omega$ may indeed be dramatically different from those of bulk metals.

While we obviously have many suggestions from theory, the answers to many of the questions raised earlier will always be based on experimental facts. The aim of experimentalists in this area is to provide laboratory conditions whereby a variety of cluster properties can be observed from high-purity, stable particles with a very narrow size-distribution. Therefore, the rate-determining step to major theoretical innovation in this area relies heavily—one might even say completely—on the synthesis, characterisation and investigation of high-purity divided metal samples. In the following sections we present a very brief overview of a variety of experimental systems currently under investigation. Here, the emphasis is on solid state materials, and a strong leaning towards the study of these systems *via* magnetism, magnetic resonance and electron microscopy.

PROBING THE ELECTRONIC STRUCTURE OF DIVIDED METALS

In order to handle and study Divided Metals they must clearly be prevented from accidentally interacting with themselves or any other substance which might perturb their properties. In this section we outline just a few methods of¹⁵ realizing this aim.

Phonon Softening in Metal Particles

The electrical resistivity of an ideal (bulk) metal has been calculated by Ziman¹⁶

$$\rho = C \frac{T}{\Theta_D} \int_0^{\Theta_D/T} \frac{x^5}{(e^x - 1)(1 - e^{-x})} dx = C \frac{T}{\Theta_D^2} \mathcal{Q}(\Theta_D/T) \quad (2)$$

This is the well known Bloch-Grüneisen equation defining the Grüneisen function¹⁷ $\mathcal{Q}(\Theta_D/T)$, where C is a constant depending on the metal and Θ_D is the Debye temperature. This describes the electron-phonon scattering process which causes transitions between k -states and hence gives rise to electrical resistivity in the bulk metal. It is therefore possible to define a reduced resistivity $\rho_T/\rho_{T\Theta_D}$ given by¹⁷ $\rho_T/\rho_{T\Theta_D} = 1.056 (T/\Theta_D) \mathcal{Q}(\Theta_D/T)$ where ρ_T , $\rho_{T\Theta_D}$ are, respectively, the ideal

resistivities at temperatures T and Θ_D . Fig 6 shows a plot of the experimentally measured electrical resistivity of bulk potassium metal (filled squares) and the theoretically predicted variation of $\rho_T/\rho_{T\Theta_D}$ via the Bloch-Gruneisen relation.

As one can see there is excellent agreement between the observed and theoretical resistivity behaviour. One might ask, therefore, "How does this description of the electron-phonon interaction survive as we successively fragment a bulk metal into small particles?" (Fig 2). To investigate this, we consider direct conductivity measurements on fine particles of Al and Ag, as well as conduction electron spin resonance (c.e.s.r.) measurements on the alkali metal colloids.

We turn first to the measurements on Al and Ag.

An alternative representation of resistivity data at various temperatures involves treating the Debye temperature Θ_D as a floating (temperature-dependent) parameter. In this way, Θ_D can be derived from resistivity measurements by fitting the experimental data to the Bloch-Gruneisen function. Ohshima *et al.*^{18,19} have reported resistivity measurements on Al and Ag particles with diameters down to 100 Å. Their data are reproduced in Fig 7 with the appropriate values of Θ_D .

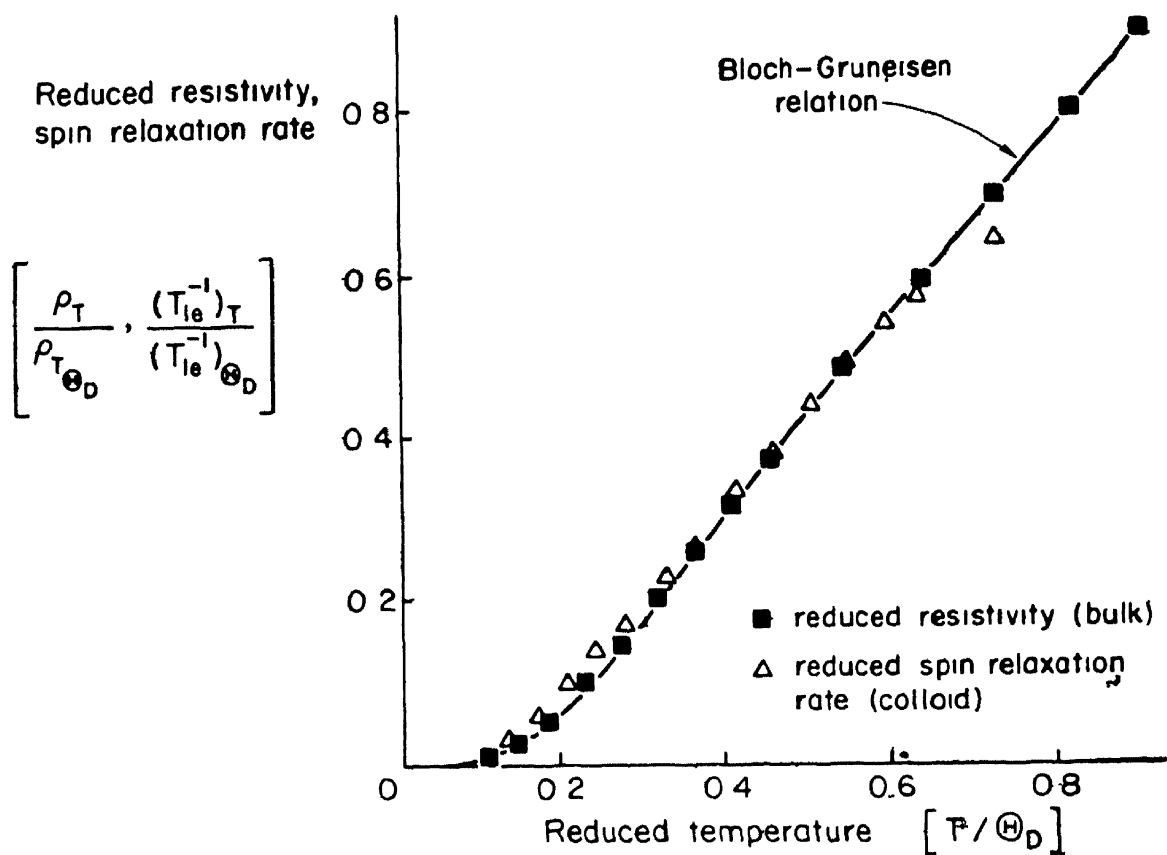


FIG 6 The duality of electron spin and resistivity scattering in bulk and colloidal potassium. A plot of the experimental reduced electrical resistivities and spin-relaxation rates against reduced temperature for potassium. The solid line is the theoretical Bloch-Gruneisen relation (eq 2).

Phonon Softening in Divided Metals

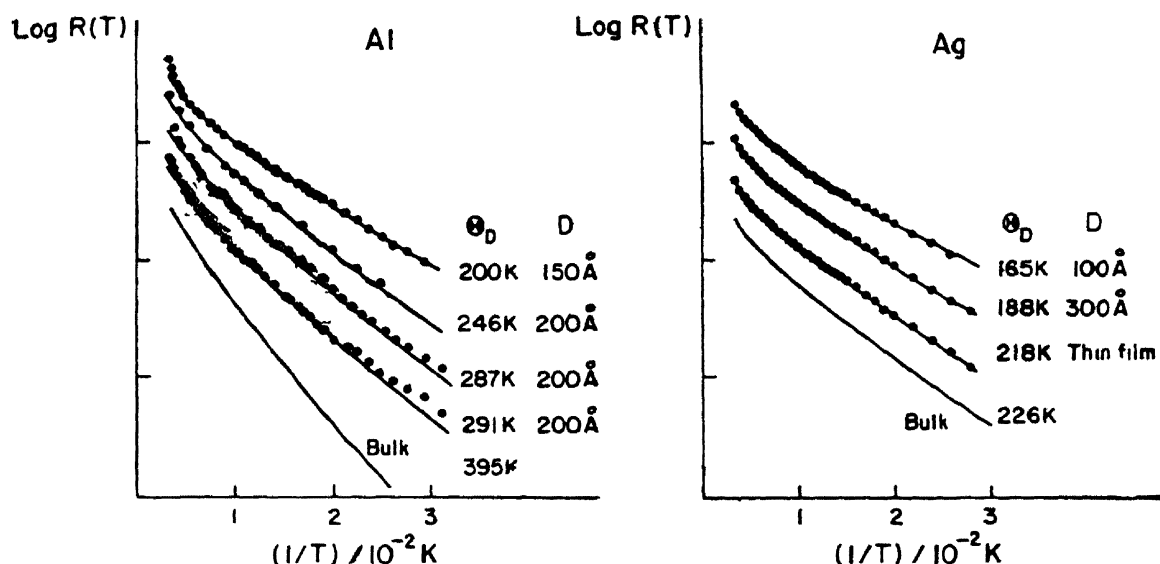


FIG 7 Phonon softening in small particle samples of Al and Ag. The plot shows the experimental resistance of the samples as a function of T^{-1} , for various particle sizes (D). The derived (eq. 2) Debye temperatures are also shown.^{18,19}

from experiment, in each case, the solid line is the theoretical resistivity variation (from eq. 2) using the suitable Debye temperature (shown also).

This lowering of the Debye temperature or "phonon-softening" in small metallic particles has been observed in a variety of systems. It has been suggested that the phonon spectra of a small particle is modified from that of the bulk metal in two ways; a low frequency cut-off due to the restriction of a finite particle size and a general lowering of phonon frequencies due to the weaker vibrational potential of the surface atoms.

Another technique for directly probing the electron-phonon interaction is c.e.s.r., recent studies on alkali metal colloids^{20,21}—respectively large with $D \sim 1000$ – 1500 Å —rely on the apparent duality of both electron-phonon and spin-phonon interactions in metals.

Elliott's²² relation between the phonon spin-lattice relaxation rate T_{1e}^{-1} and the corresponding resistivity relaxation rate τ_R^{-1} (which is proportional to the electrical resistivity) is

$$T_{1e}^{-1} = T_{2e}^{-1} = \alpha (\Delta g)^2 \tau_R^{-1}, \quad (3)$$

where α is a numerical constant and Δg is the deviation of the observed electron g -factor from the free spin value (2.00231).

It was suggested by Yafet²³ that T_{1e}^{-1} may also be described by the Bloch-Grüneisen function (eq. 2) with a different constant C which now involves its matrix

elements of the spin-orbit coupling operator between spin-up and spin-down Bloch wave functions. Yafet's²³ detailed calculations showed $T_{1e}^{-1} \propto T^5$ at low temperatures, changing to $T_{1e}^{-1} \propto T$ at high temperatures. This prediction for the c e s r. case is observed for the corresponding temperature dependence of the electrical resistivity in a wide range of metals. To illustrate this duality in both electron spin and resistivity scattering processes²¹ in the alkali metals and colloids, we show in Fig 8 the intrinsic electron spin relaxation rates in sodium, potassium and rubidium colloids ($D \geq 10^3 \text{\AA}$) as well as the corresponding electrical resistivities of the bulk metals. Note also that c e s r. data for bulk potassium are also included in Fig 8, and these are in agreement with the form of the colloidal particle results. We can see, therefore, that there are indeed clear parallels between the temperature dependence of the electrical resistivity and spin relaxation rates for these three metals. From eq. 2 it is also possible to define a reduced (intrinsic) spin relaxation rate $(T_{1e}^{-1})_r / (T_{1e}^{-1})_{\text{D}}$, in analogy to the reduced resistivity (Fig 6), where the subscripts denoted a temperature T and the Debye temperature, respectively. Since Δg is temperature independent, eq 2 indicates that the similarly defined reduced spin relaxation rate should be described by the same Bloch-Gruneisen function. In Fig 6, these quantities are plotted both from resistivity and c e s r. measurements on potassium (bulk and colloidal samples) along with the function defined by eq 2 assuming a Debye temperature of 110 K.

One can adopt a similar procedure to that outlined for resistivity measurements for processing the electron spin relaxation data, namely, treating the Debye temperature

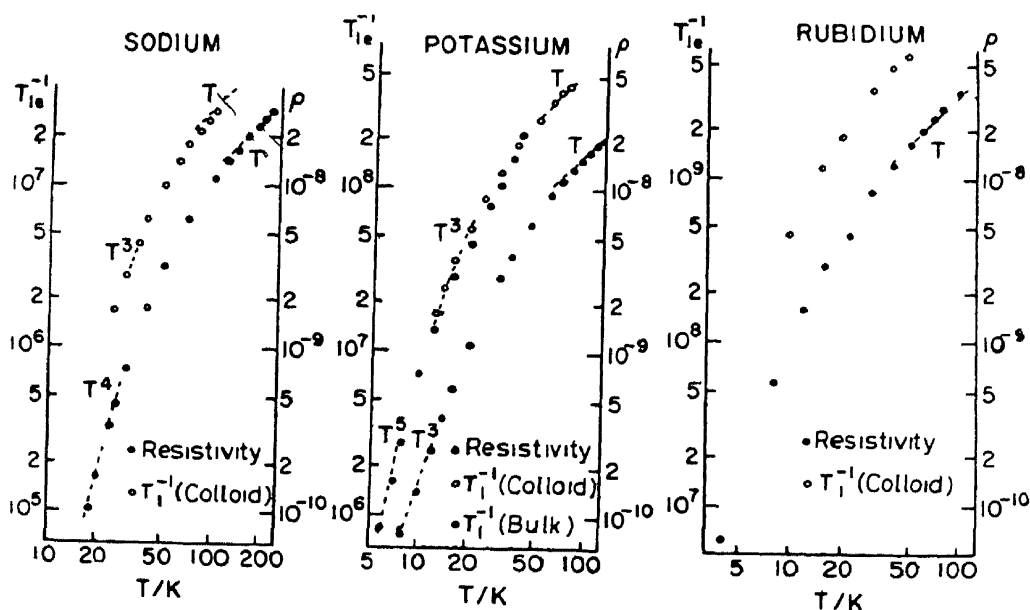


FIG 8 The temperature dependence of the intrinsic electron spin-spin relaxation rates as a function of temperature for sodium, potassium, rubidium and caesium colloids. Also included is the corresponding temperature dependence of the ideal electrical resistivities for these metals. In all cases the temperature exponent is indicated (Ref. 21)

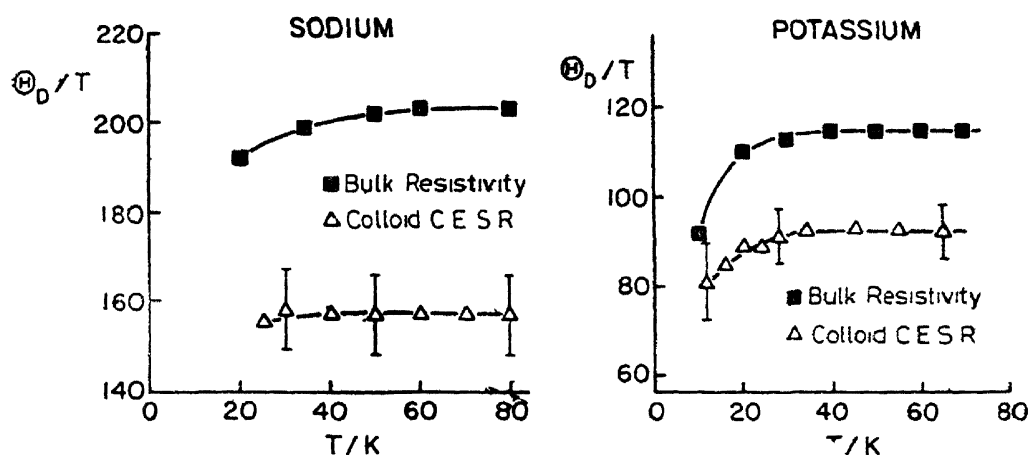


FIG 9 Experimental Debye temperatures for sodium and potassium derived from bulk electrical resistivity and colloidal c e s.r. measurements. Note the decrease in Θ_D for the colloidal particles (Ref. 21)

as a temperature-dependent parameter and evaluating the characteristic temperatures from the resistivity and spin-relaxation data, respectively. The results for sodium and potassium are shown in Fig 9. Once again, one sees a reduction in the Debye temperature or "phonon softening" in these small metallic particles. It is interesting to note that this reduction is Θ_D for both the alkali samples,^{20,21} and those of Al and Ag^{18,19} (Fig. 7) appears to be a smooth function of D , for diameters down to 150 Å (in the case of Al) and 100 Å (in the case of Ag). However, we once again raise the question of the microscopic nature of the Al, Ag samples; namely, the considerable difficulties of actually measuring electrical resistivities for very small samples which may well be more representative of a percolation problem²⁴. Similar problems may also pervade the c.e.s.r. studies on quenched metal solutions, but it is interesting to note that there does appear to be a rather impressive adherence to the Bloch-Grüneisen function for particle sizes down to approximately 50 Å.^{25,26} This suggests that only minor changes occur in the gross details of the lattice (phonon) spectrum of these divided metals for dimensions down to the onset of the quantum size-effect regime.

Ionic and Metallic Species in Zeolites and Vycor

A large number of inorganic materials contain regular cavities or vacancies forming networks or parallel channels. In zeolites the size of the cavities is typically in the range from 2–12 Å. Within these cavities metal clusters and particles can be sorbed or produced *in situ*. In addition, the availability of several types of zeolites means that different three-dimensional arrangements of cavities can be investigated for preparing and stabilizing small metallic particles. In recent work^{27,28} we have concentrated on faujasitic zeolites in their sodium, potassium and rubidium-cation exchanged form. A representation of the structure of faujasitic zeolites is given in Fig 10.

The polyhedron with 14 vertices (tetrakaidecahedron) in Fig 10 is known as the sodalite or β -cage and is the principal building block of the 3 structures shown

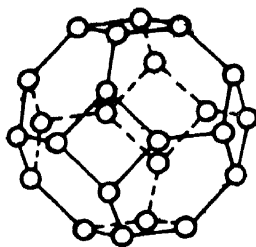
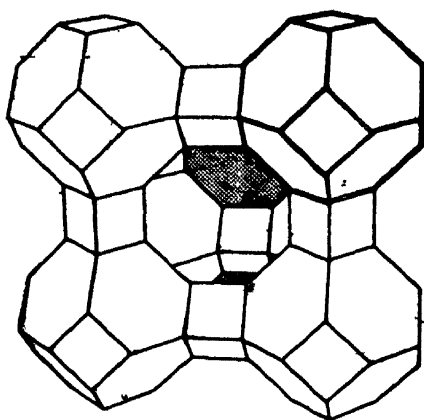
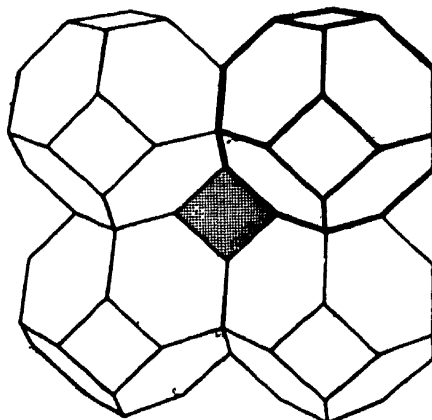
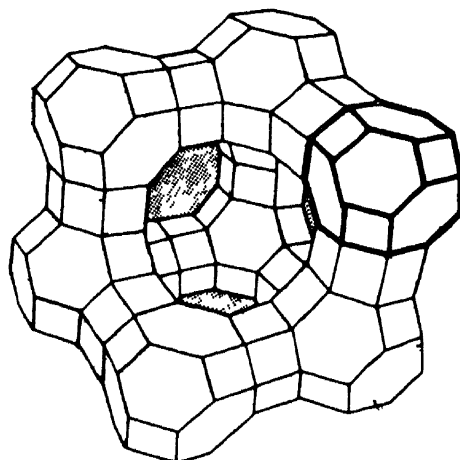
**Truncated octahedron****Zeolite A****Sodalite****Faujasite (zeolites X and Y)**

FIG 10 The sodalite cage and the structure of zeolites belonging to the faujasite family. The framework oxygen atoms and exchangeable cations are not shown

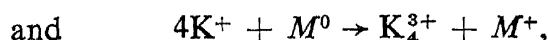
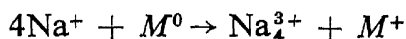
in the figure Only one type of cavity occurs in sodalite, with a diameter of $6.5\text{\AA}$ and accessed through small 6-membered pores some $2.2\text{\AA}$ in diameter There are approximately 6 alkali metal cations in each sodalite cage

Zeolite A is a synthetic mineral with no natural counterpart. The sodalite cages are connected by double four-membered rings, forming an interconnected set of larger cavities within the material known as α -cages with a diameter of $11.5\text{\AA}$ and accessed through eight-membered pores $4.2\text{\AA}$ in diameter. There is one α -cage for every sodalite cage and 12 alkali-metal cations are distributed between them.

Zeolites *X* and *Y* are the synthetic counterparts of the naturally occurring mineral faujasite. Here the sodalite cages are connected by double six-membered rings forming an interconnected set of even larger cavities within the material known as α -cages (or supercages) with a diameter of $12.5\text{\AA}$ and accessed through 12-membered pores $7.5\text{\AA}$ in diameter.

Two distinct species can be formed following the reaction of, for example, Na^+ -exchanged Zeolite *Y* with the vapour of sodium, potassium, rubidium or caesium metals^{27,28}. The relative amount of the two species can be changed by varying the concentration of the alkali vapour.

Ionic Clusters in Zeolites The exposure of Na^+ -Zeolite *Y* to a low concentration of alkali vapour results in brightly coloured samples whose electron spin resonance (e.s.r.) spectra are characteristic of the ionic cluster, Na_4^{3+} . This species consists of an unpaired electron interacting with 4 equivalent sodium nuclei (^{23}Na , $I = 3/2$, 100 per cent abundance). Similarly, the reaction of K^+ -Zeolite *Y* with alkali vapour gives rise to the corresponding potassium species K_4^{3+} . The e.s.r. results^{27,28} are summarized in Fig. 11. Interestingly, no e.s.r. signals indicative of Rb_4^{3+} clusters were ever found in corresponding reaction with Rb^+ -exchanged Zeolite *Y*. Thus, the reactions of Na^+ - and K^+ -exchanged Zeolite with low concentrations of alkali metal vapour can therefore be written (in a manner formally akin to the formation of an F-centre) as



where M^0 represents the vapour of sodium, potassium or rubidium. The available evidence to date suggests that the ionic M_4^{3+} clusters are almost certainly accommodated within the sodalite cages (β cages) in the structure, as shown in Fig. 12. We believe that the rubidium ionic cluster Rb_4^{3+} either does not form at all, as it is unstable to disproportionation with respect to small metallic particles. Specifically, computer simulations (shown in Fig. 13) suggest that geometrical/spatial considerations may well form the most important feature in inhibiting Rb_4^{3+} formation in the sodalite cage. Consistent with this, we note the difficulty in routinely exchanging Na^+ cations in Zeolite-*Y* for the corresponding Rb^+ cations.

Metallic Clusters in Zeolites: Exposure of Zeolite samples to a high concentration of alkali vapour results in dark-coloured (generally blue/black) samples with an e.s.r. signal characteristic of small metallic particles. These may also be initially located within the sodalite cages, but at high (metal) doping levels we have assumed that the large "metallic" clusters are accommodated within the α -cages (Fig. 10).

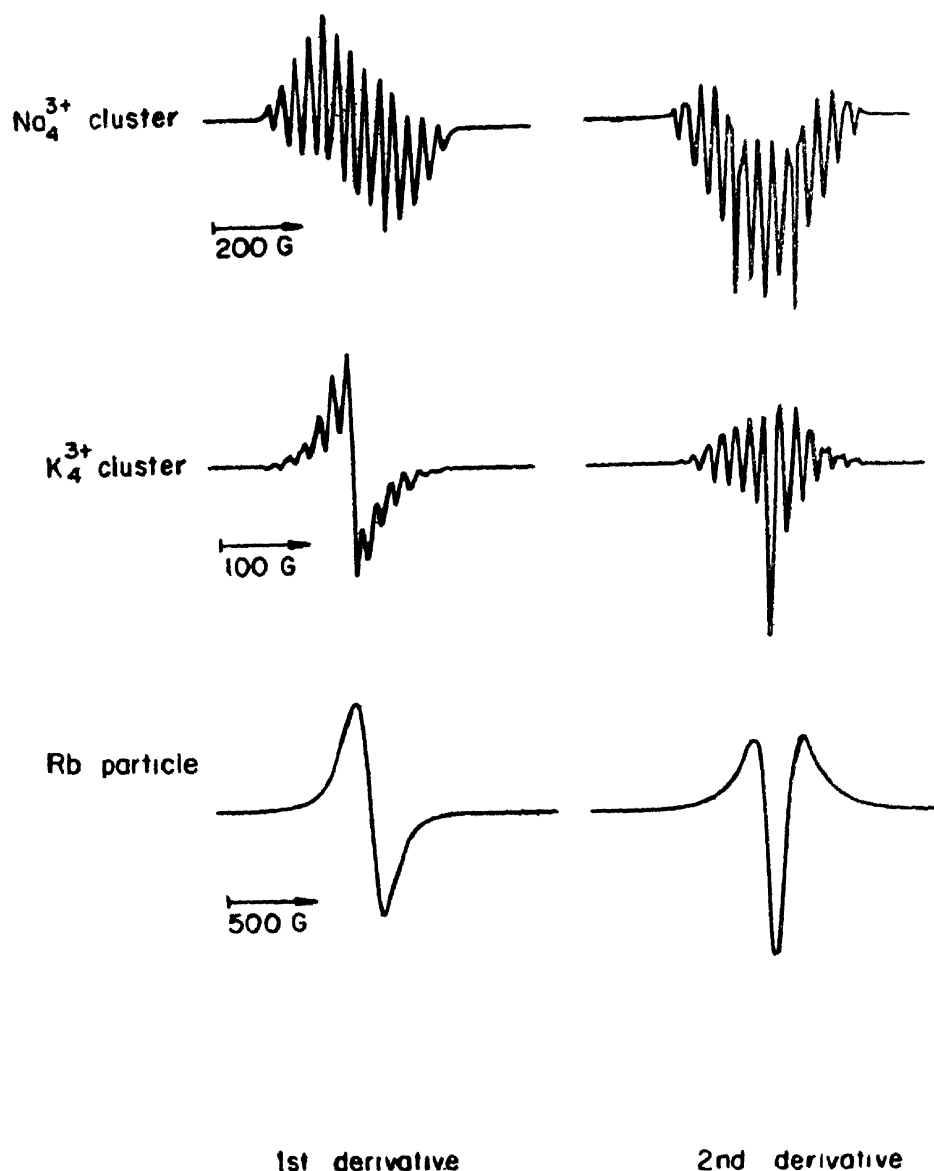


FIG 11 ESR spectra of alkali-doped zeolite Y samples, showing both 1st and 2nd derivative spectra. Here we show the Na_4^{3+} cluster in zeolite $\text{Na}^+ - \text{Y}$, the K_4^{3+} cluster in zeolite $\text{K}^+ - \text{Y}$ and the rubidium metallic cluster observed in $\text{Rb}^+ - \text{Y}$ zeolite after exposure to rubidium vapour.²⁷

There is, as yet, no structural data on these metal-loaded Zeolites to confirm, or refute this suggestion.

As we have noted in Sec II 2, and III, 1 the electron spin relaxation rate in metal particles depends critically upon their size. If the particles are sufficiently large such that $\Delta \ll g_e \mu_B H$ (Fig. 5), the electron-spin surface scattering rate (and hence the e.s.r. line width) should vary inversely with the diameter of the particles. Here, spin-phonon scattering closely follows the Bloch-Grüneisen law (Figs 6, 8) and the magnetic susceptibility follows a Pauli-type, temperature-independent paramagnetism. Conversely, if $\Delta \gtrsim g_e \mu_B H$, then both surface scattering and phonon-scattering mechanisms are quenched. Thus, relatively narrow e.s.r. signals can be

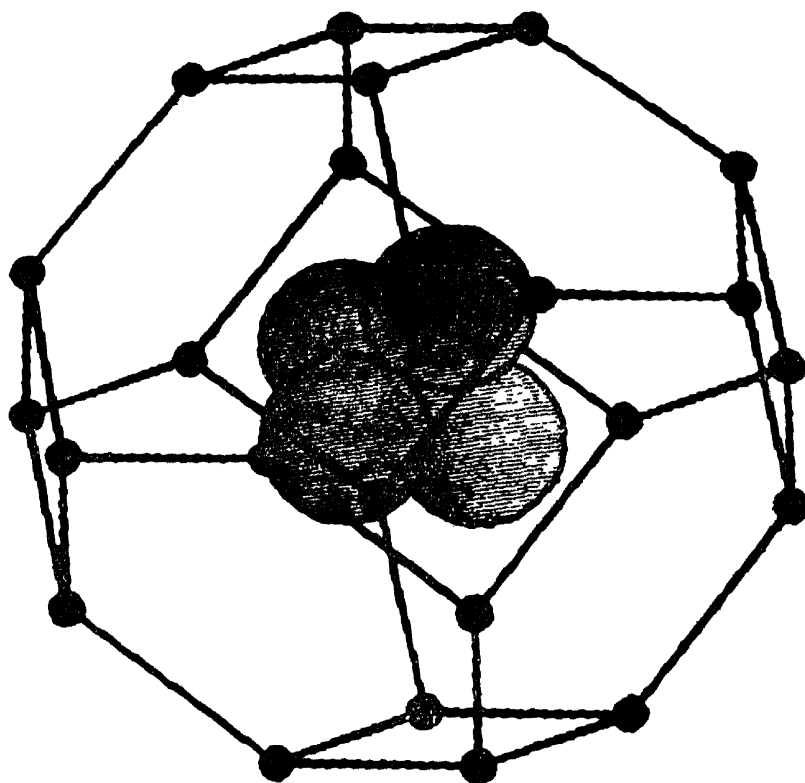


FIG 12 An illustration of a sodalite cage containing a Na_4^{3+} cluster of (presumed) tetrahedral geometry ²⁷

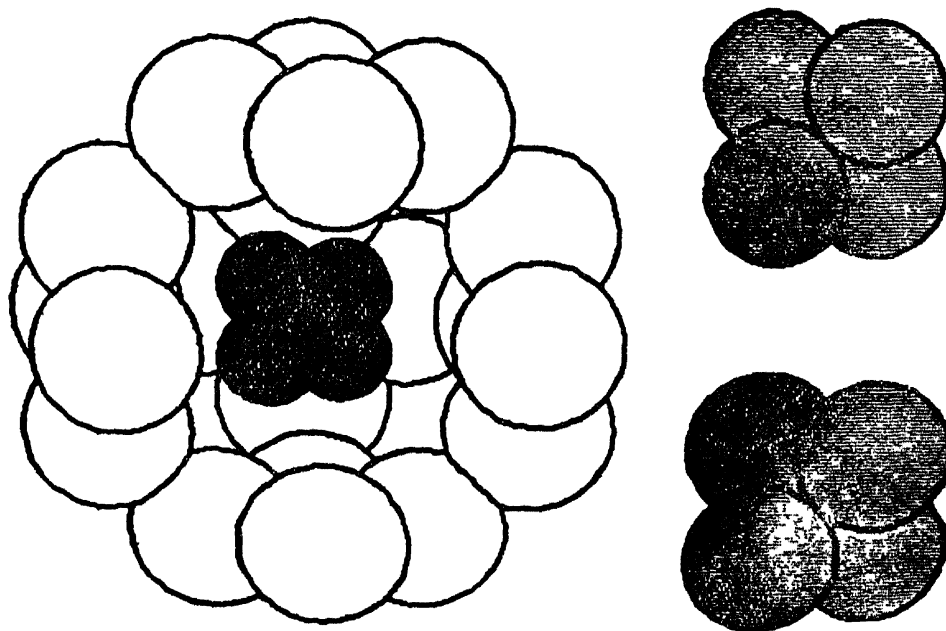


FIG 13 A scale view of a Na_4^{3+} cluster within a sodalite cage. Top right, a K_4^{3+} cluster drawn to scale. Bottom right, a hypothetical Rb_4^{3+} cluster ²⁷

observed at comparatively high temperatures ($T/\Theta_D \gtrsim 0.5-1.0$), even in the heavier metals²⁹ for which spin-orbit coupling constants are very large. In addition, the

paramagnetic susceptibility of the particles is expected to follow a Curie-type variation with temperature.

This quantum size-effect was predicted to occur in sodium particles smaller than $100\text{\AA}$, which is certainly much larger than the particles postulated to be in the Zeolite cavities. Therefore, it has been suggested that the "metallic" e.s.r. signals observed in the concentrated samples are characteristic of small particles of alkali metal located within the Zeolite cavities. As expected, the electronic g -factors of the metallic particles (Table I) highlight the very great importance of the spin-orbit interaction in the heavier metals. Most striking, the particles of the heavier metals K, Rb and Cs appear to be small enough to quench the usual rapid spin-relaxation mechanism operative in bulk samples of these elements. A possible explanation relies on the relative size of the atoms; more sodium atoms can obviously fit into the Zeolite cavities than can rubidium atoms. Thus the sodium metallic particles possibly contain more atoms than their rubidium counterparts and hence have properties more similar to the large, colloidal samples discussed earlier (III 1). Our recent Faraday susceptibility experiments³⁰ reveal that heavily loaded sodium samples (for which the "small metallic particle" e.s.r. was observed) show a paramagnetic susceptibility behaviour which follows a Curie-type variation with temperature. These metal-loaded Zeolites may therefore be ideal materials to study the unusual electronic properties of small metallic particles

TABLE I

Electronic g -values for alkali metal particles in Zeolites and Vycor

Metal	Particles in Vycor ^a	Particles in Zeolites ^b	Bulk Metal
Sodium	1.996 ± 0.001	1.9997	2.0015
Potassium	1.999 ± 0.001	1.9978	1.9997
Rubidium	1.988 ± 0.001	1.989	1.9984
Caesium	2.010 ± 0.03	—	2.013

^a ref 31

^b ref 28

Similarly, we have recently investigated the use of porous "Vycor" glass as a supporting matrix for silver and alkali metal particles. This glass is perforated with channels between 40 and $70\text{\AA}$ in diameter, and thus contain larger cavities than in Zeolites. We have reported a variety of methods of preparing Vycor-supported silver particles, as well as alkali metal colloids supported by Vycor glass. The g -values for one sample each of sodium, potassium, rubidium and caesium are given in Table I. The g -values in Table I are indeed very similar to those of metal particles in Zeolite-Y and in some cases differ significantly from the bulk values (which are also given for comparison)

Transition Metal Cluster Compounds

There exists a wealth of well characterized metal-cluster complexes³ which are ideal candidates for the study, amongst other things, of the genesis of "metallic" properties from the molecular regime.³² These clusters generally have a polynuclear, metal-metal bonded core and a tightly bound outer ligand covering of, for example, CO molecules. Thus, the cluster carbonyls of various transition elements have been shown by X-ray crystallography to exhibit many different geometries. These compounds represent cluster fragments effectively isolated from adjacent cluster units by inert sheaths of carbonyl ligands. In Fig 14, we show a representation of the typical metal atom geometries in transition-metal carbonyl clusters.³²

A recent study of magnetism in the cluster compounds of osmium begins to shed light on the evolution of certain aspects of what one might term "metallic" behaviour. Johnson *et al*³² report measurements of the magnetic susceptibilities of a series of cluster compounds of osmium (Fig. 15) over the temperature range 1.5–300 K. With the exception of the hydrido cluster $\text{H}_2\text{Os}_{10}\text{C}(\text{CO})_{24}$ the magnetic susceptibilities of the entire series of clusters were rigorously temperature independent down to 1.5 K. It is possible to estimate from these data the excess paramagnetic molecular susceptibilities after allowing for the ion-core and ligand contributions.³² The observed susceptibilities (Fig 15) are most naturally interpreted as arising from a Van Vleck paramagnetic contribution to the susceptibility. This modification arises from the modification of the cluster wavefunction caused by the external magnetic field. The modified wave function is described by the admixture of excited states in which electrons are 'promoted' from occupied bonding orbitals to the first unoccupied (antibonding) levels. The increase in this Van Vleck paramagnetism (Fig 16) suggests that the characteristic energy gap separating filled from vacant orbitals decreases with increasing cluster size. Note also in Fig 15 that the high nuclearity cluster $\text{H}_2\text{Os}_{10}\text{C}(\text{CO})_{24}$ behaves in a rather different fashion, showing a marked temperature dependence in the susceptibility at low temperatures. Obviously, paramagnetic impurities can play havoc with any interpretation of genuine (i.e. intrinsic) paramagnetism. In the study of osmium cluster carbonyl, strenuous efforts were made to eliminate possible paramagnetic contaminants. In addition, recent studies of the magnetic behaviour of high nuclearity platinum clusters³³ and "Cherry" crystallites³¹ [e.g. $\text{Ni}_{38}\text{Pt}_6(\text{CO})_{48}\text{H}_{6-n}]^{n-}$ ($n = 5, 4$) ions show unusual magnetic behaviour.

It is interesting to question theoretically how the Van Vleck paramagnetism is modified as the characteristic HOMO-LUMO energy gap changes^{32,35}. We take the molecular cluster as having no magnetic moment in the ground state (as required by most bonding models). Suppose there is a non-diagonal matrix element $(n|\mu_z|0)$ of the magnetic moment operator, connecting the ground state D with the excited state n of energy $\Delta = E_n - E_0$ above the ground state. Then by standard perturbation theory we see that the wave function of the ground state in a small field ($\mu_z H \ll \Delta$) becomes³⁵

$$\psi_0 = \psi_0 + \frac{(Hn|\mu_z|0)}{\Delta} \psi_n$$

Typical Metal Atom Geometries in Cluster Carbonyls

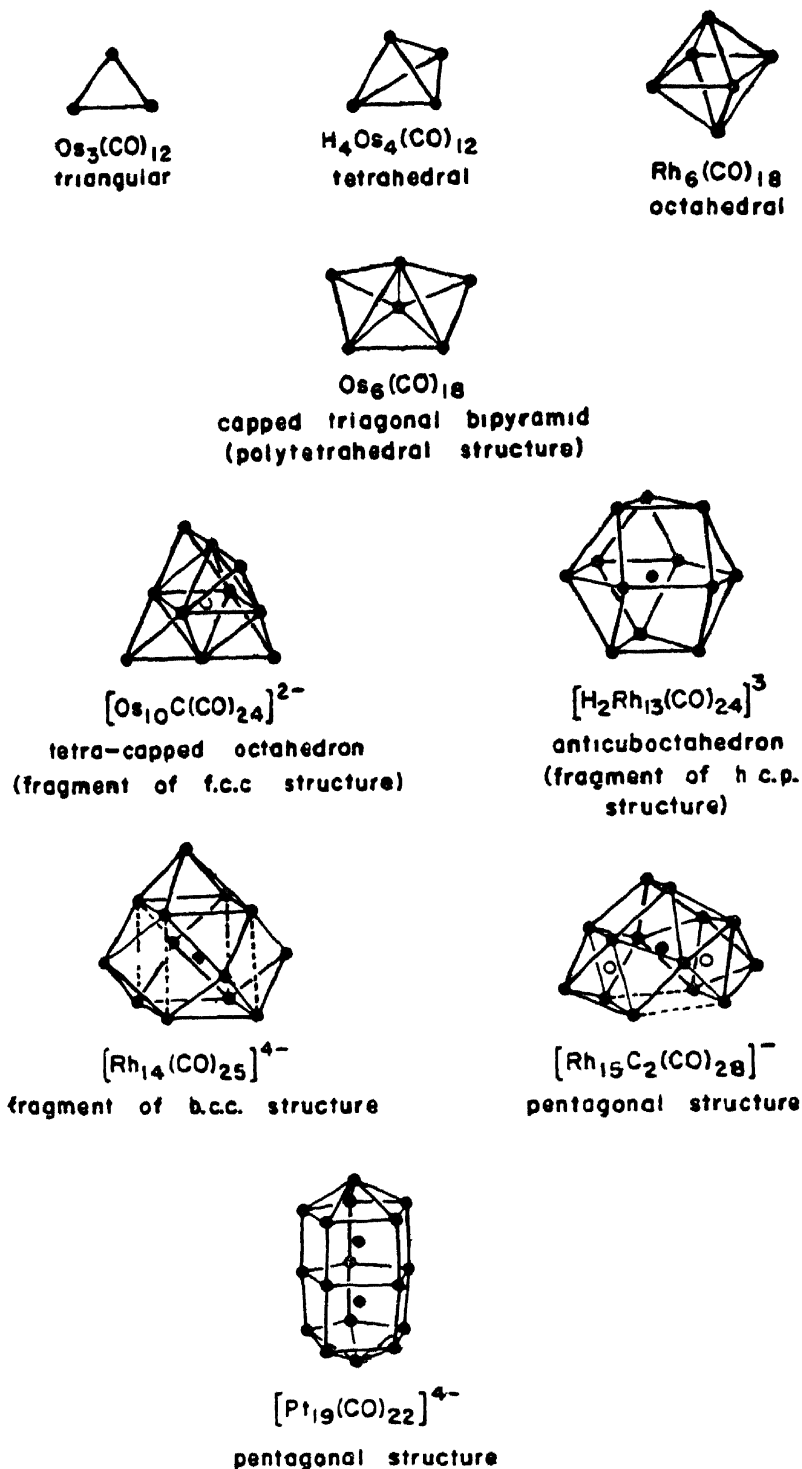


FIG 14 A representation of the typical metal atom geometries in transition metal carbonyl clusters. For clarity, the carbonyl ligands have been omitted. The open circles denote interstitial C atoms in the cluster ³²

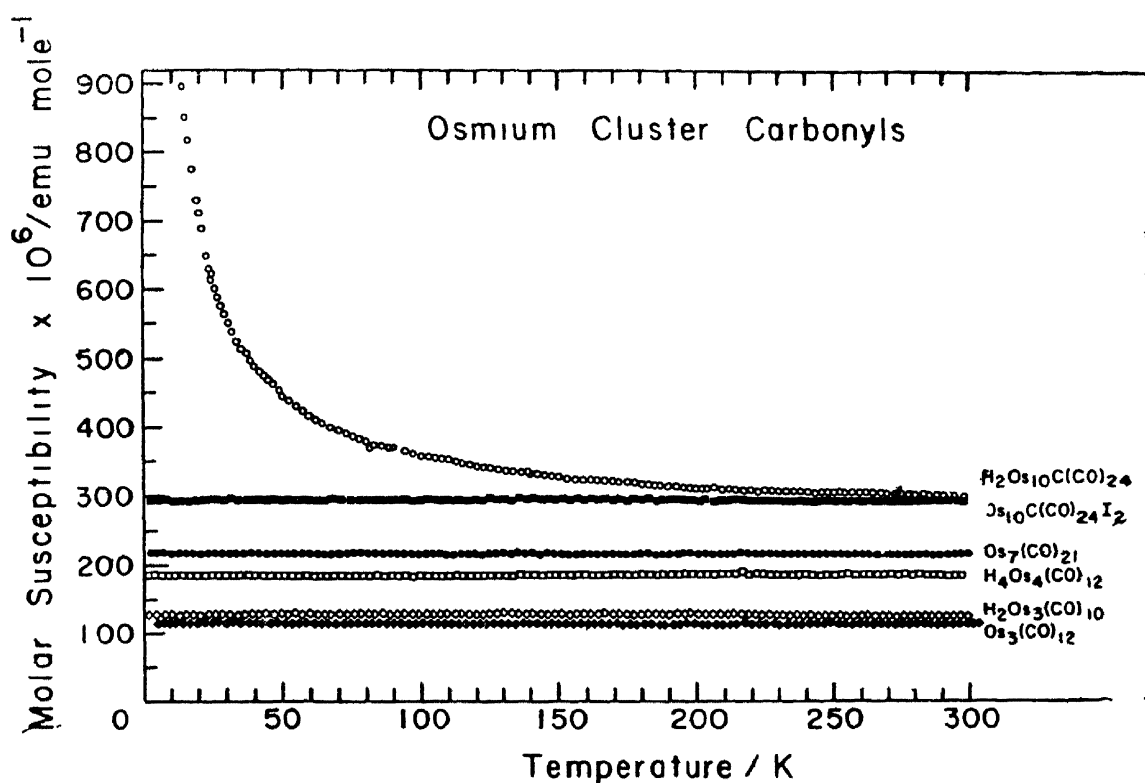


FIG 15 The excess molecular susceptibility in osmium cluster carbonyls.

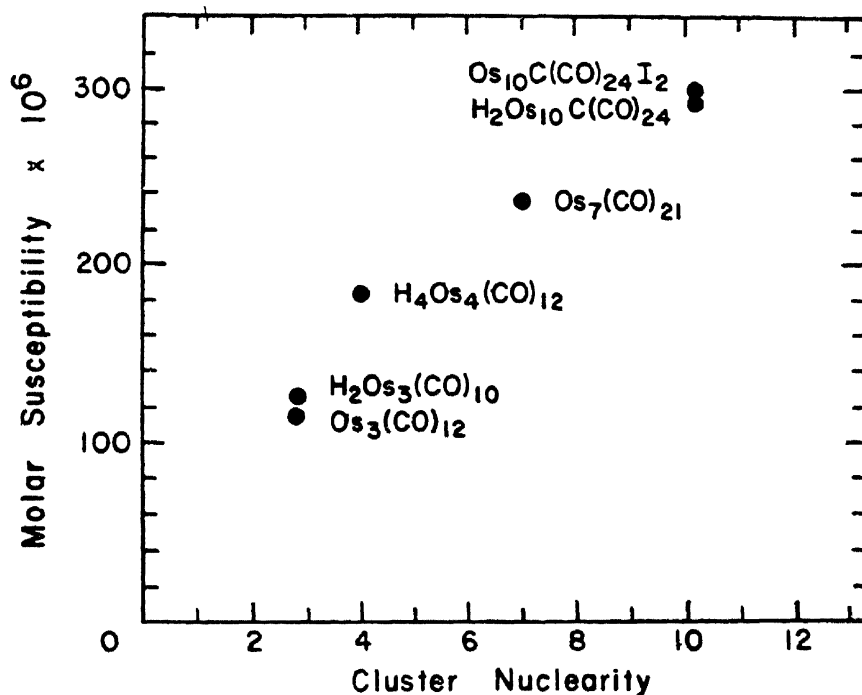


FIG 16 Paramagnetism in osmium cluster carbonyls, the variation of the high temperature (298 K) excess molecular susceptibility for osmium cluster compounds of increasing nuclearity³²

and the wavefunction of the excited state becomes

$$\psi'_n = \psi_n - \frac{H(O | \mu_z | n)}{\Delta} \psi_0$$

The upper state then has a moment

$$-2H | (n | \mu_z | O) |^2 / \Delta$$

The total (induced) magnetic moment in the system is now

$$\mu_{total} = \frac{(n | \mu_z | O) \{1 - (\exp(-\Delta/kT))\}}{1 + (\exp(-\Delta/kT))}$$

Consider two limiting cases

(a) $\Delta \ll kT$

The surplus population in the ground state is approximately equal to $N\Delta/2kT$, where N is the Avogadro number, which gives for the susceptibility,

$$\chi = \frac{N | (n | \mu_z | 0) |^2}{kT}$$

This contribution is of the usual Curie form, although the mechanism of magnetization here is through polarization of the states of the system, whereas with "free" spins the mechanism of magnetization is the redistribution of ions among the states

(b) $\Delta \gg kT$

The population now is almost nearly all in the ground state, so that the susceptibility is, summed over all suitable states n ,

$$\chi = 2N \sum_n \frac{| (n | \mu_z | 0) |^2}{E_n - E_0}$$

and independent of temperature.

Thus, the observed (Fig 16) increase in the Van Vleck paramagnetism in the larger clusters may in part, be associated with the gradual diminution in $E_n - E_0$

Finally, it is interesting to speculate³⁵ on the most noticeable lack of nuclear magnetic resonance (nmr) observations on the large platinum (and other) molecular clusters³⁴. The possible occurrence of such a large (induced) paramagnetism will give rise to a concomitant paramagnetic contribution to the nmr chemical shift³². This, for nuclei in a fairly low symmetry environment, relaxation via chemical shift anisotropy may well be extremely efficient in these large clusters, leading to excessive nmr line broadening

Colloidal Metals Revisited

This paper was begun with a brief reference to Faraday's remarkable observations¹ on the nature of colloidal gold as a Divided Metal. In this final section, I

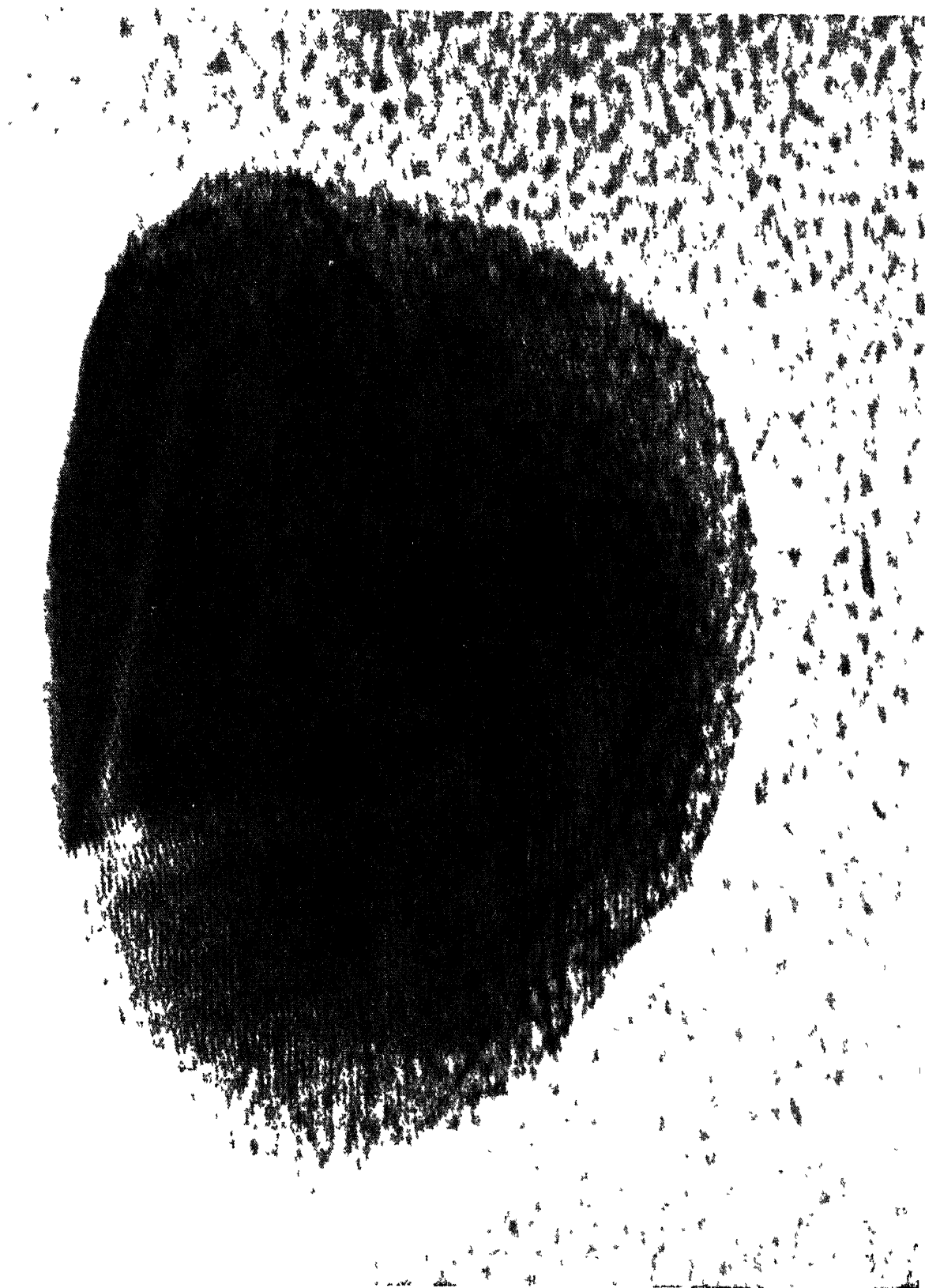


FIG 17 A high resolution electron microscope photograph of an individual gold particle ²

will give a brief mention of more recent studies on colloidal gold^{2,36} My aim here is to show how key experiments on this old and venerable area of Chemistry are now possible given the considerable power and utility of High Resolution Electron Microscopy^{37,38}

Colloid Chemistry is one of the oldest branches of the chemical sciences, once thought by many to be past its zenith Within this last decade, however, there has been a powerful renaissance of interest in the subject, particularly as regards the chemical and physical properties of colloidal aggregates of small metal particles These colloidal particles represent a domain of matter intermediate between the bulk, macroscopic metallic state and the microscopic world of atomic and molecular clusters (Fig 2)

Fig. 17 shows a high resolution micrograph of a colloidal gold particle of diameter 50–55Å. Here the atomic planes in the constituent twinning particles may possibly be now identified^{2,36} Such investigations will, I feel, lead to a detailed microscopic picture of the composite topology of colloidal particles Our initial work suggests that the colloidal particle is a collection of intergrown subcomposites In these systems, the electronic scattering time τ_R may be dominated by a scattering length determined by the single, subcomposite dimension, rather than by the much larger colloidal dimension This “cluster” composite view has recently been

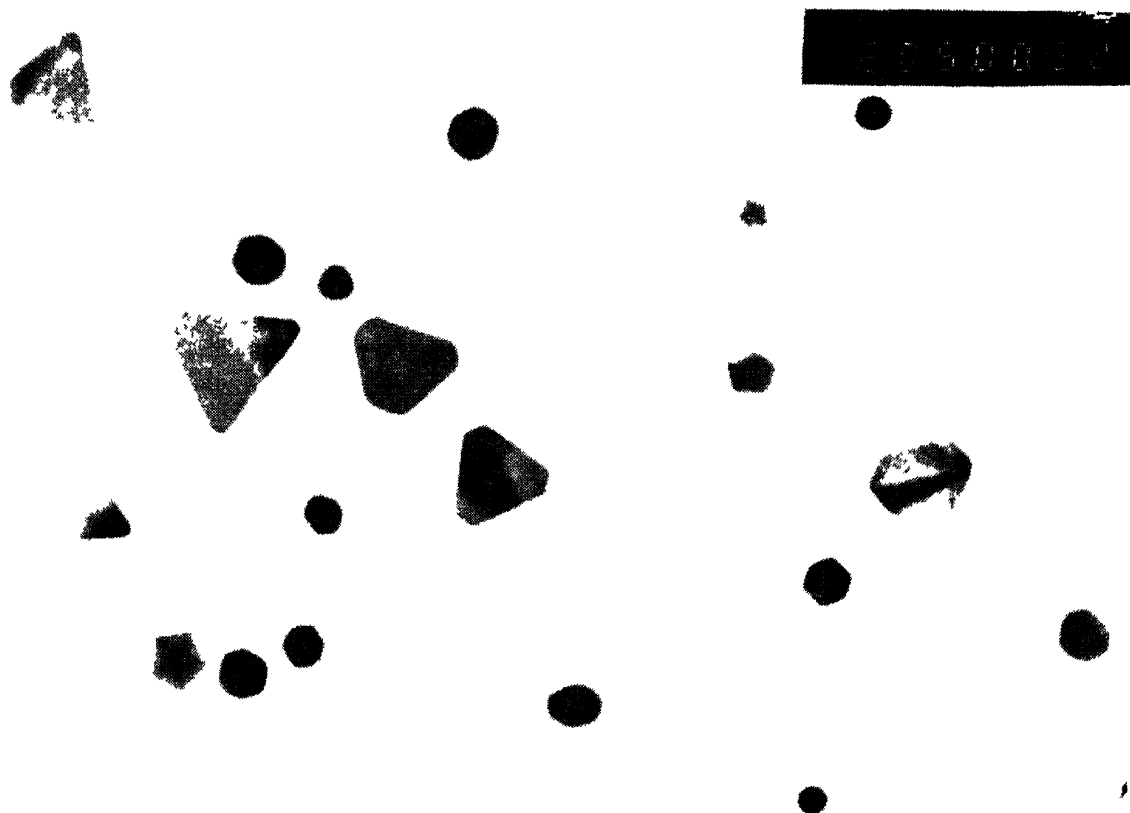


FIG 18(a) Transmission electron microscope photographs of (a) gold “trigons”

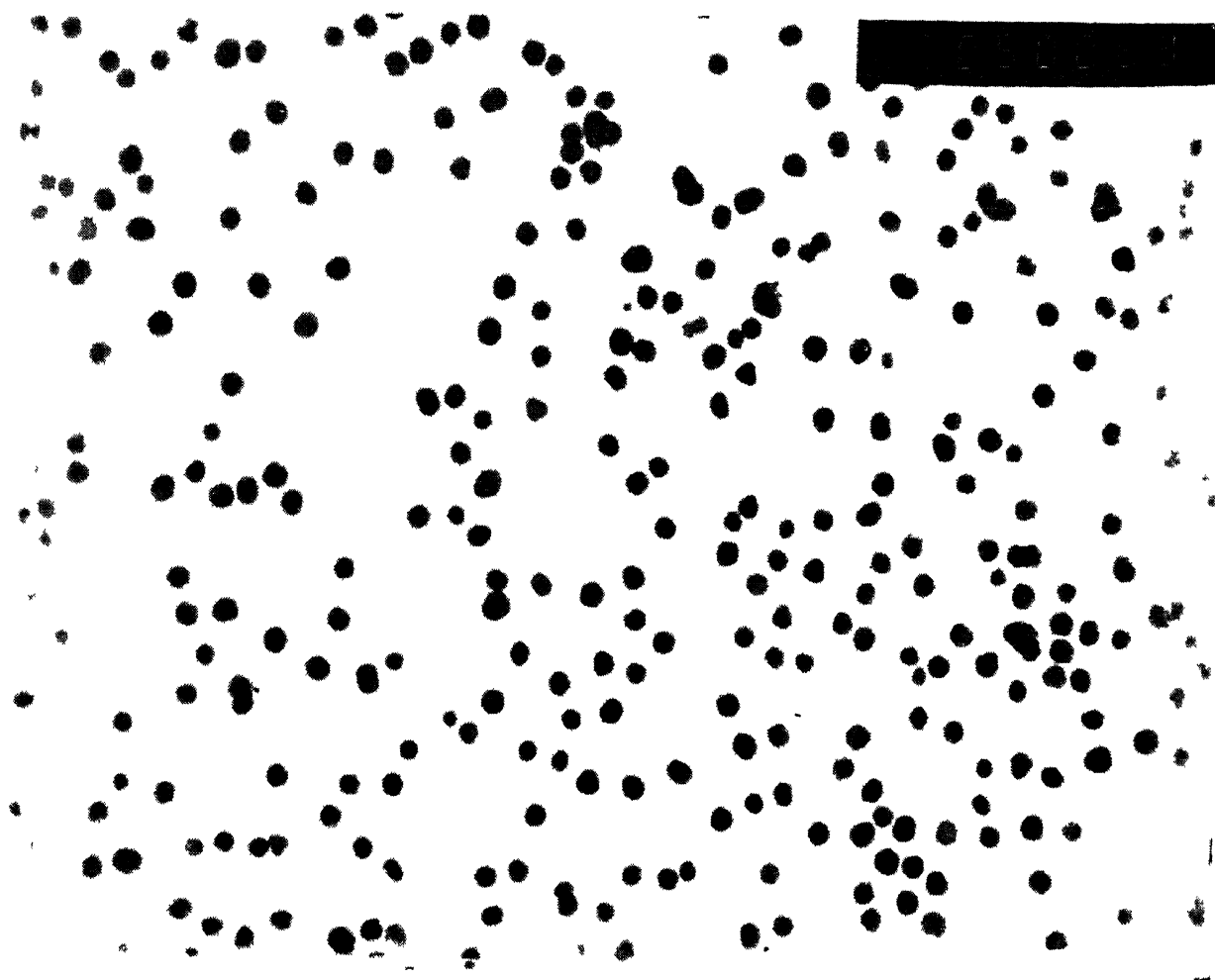


FIG. 18(b) Spherical particles

advanced by Curtin and Ashcroft¹² to account for far-infrared absorption coefficients in small particle systems. Colloidal gold can also be formed as pentagonal bipyramidal particles. Fig. 18 shows gold sols prepared in our laboratory both by citric acid (platelets) and sodium citrate (spherical particles) routes. The conditions for both preparations are identical (the same volume of 1 per cent solution of each reducing agent added). One's hope is ultimately to develop morphology-selective preparations of small gold particles.

One must conclude that, just as in Faraday's day, attempts to characterize and explain the physico-chemical properties of colloidal, divided metals still pose a strong challenge to experimenter and theoretician alike.

CONCLUSION

The title 'Divided Metals' is in some ways a misnomer, if the individual grain of matter is sufficiently divided, one anticipates a transition to insulating behaviour (see Fig. 3). However, I hope to have illustrated that a 'gedanken experiment'—as popularized in Fig. 2 may indeed be a reflection of genuine experimental systems.

which straddle the demarcation between the macroscopic and microscopic regimes of matter. I have noted that a reduction in the number of atoms contained within a grain of solid metal may lead to interesting changes in electronic properties due to the appearance of a respectable energy gap in an (assumed) continuum of levels. The further fragmentation of an erstwhile metal particle may lead to an even more drastic modification, namely, the cessation of metallic conductivity within the grain of matter. The precise experimental conditions for effecting the transformations (noted in Fig 2) for a single system may appear elusive. However, an examination of a variety of experimental systems allows one to assemble various 'snapshots' of each of the individual situations in¹ "a metallic divided state"

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STRUCTURE AND SUPERCONDUCTIVITY IN TERNARY SYSTEMS OF COMPOUNDS

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The structure and superconductivity exhibited by the metal excess ternary systems of compounds, with special references to the Chevrel phases, rare earth rhodium borides and transition metal phosphides are discussed, in addition to the other interesting physical properties. Cluster formation, 3d-network with simple crystal symmetry and charge transfer effects are important for the realization of high T_c superconductivity.

Key Words : Metal Excess Ternary Systems; Superconducting Compounds; Ternary Superconductors

INTRODUCTION

A ternary compound is one which contains three elements each occupying a distinct set or sets of crystallographic lattice sites and preferably one element should be a non-metal. Examples are BaTiO_3 , $\text{Y}_3\text{Fe}_5\text{O}_{12}$, PbMo_6S_8 etc. This crystallographic definition clearly distinguishes ternary compounds from binary or pseudo binary phases (e.g., $\text{Li}_x\text{Ni}_{1-x}\text{O}$, $(\text{V}_{1-x}\text{Cr}_x)_2\text{O}_3$, $\text{Mo}_2\text{Re}_4\text{S}_8$ etc.) in which only two sets of lattice sites are occupied or which contain only two species of elements. Metal excess ternary systems (METS) of compounds are those in which only part of the valence electrons are involved in bonding (say, with the non-metal) and the excess valence electrons of the metal(s) will partially fill the conduction band formed by the overlap of the requisite metal *s*-, *p*- and *d*-orbitals^{1,2}. Examples are PbMo_6S_8 , ErRh_4B_4 , $\text{Pb}_2\text{Rh}_3\text{S}_2$, ZrRuP , NbReSi etc. Thus, METS compounds invariably exhibit high electronic conductivity and metallic behaviour. Theoretical considerations reveal that superconductivity in a metallic material can occur whenever there is a large density of electronic states at the Fermi level in a partially filled conduction band (preferably a narrow band) and a favourable electron-phonon interaction. Hence, METS in principle, satisfy the requirements for the exhibition of superconductivity.

Superconductivity, the phenomenon of vanishing electrical resistivity in a substance below a certain critical temperature (T_c), is not uncommon and many metals, alloys, intermetallics, binary and ternary compounds and organic charge-transfer complexes become superconducting at low temperatures. Fig 1 gives a survey of the known superconductors. Of the more than 1000 superconductors

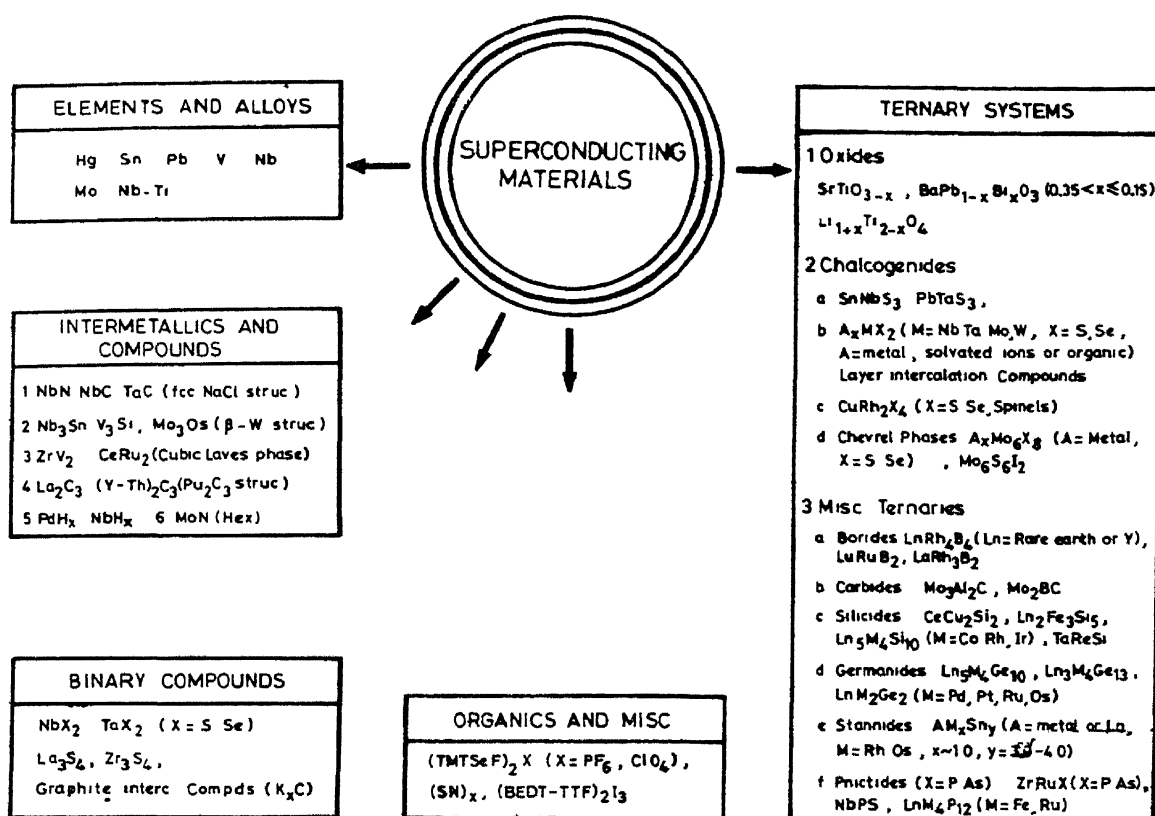


FIG 1 Survey of the known superconducting materials

known, only a handful possess T_c greater than 10 K and these are called high T_c or *high temperature* superconductors. The intermetallic binary compound Nb₃Ge has the highest T_c of 23.2 K of all the known materials whereas PbMo₆S₈ with T_c of 15.2 K is the highest known for a ternary METS compound. Since a large number of compounds are known or can be synthesized and also since chemical manipulation is easily possible in them, the METS compounds do seem to offer a better scope for the realization of high T_c and high critical magnetic field (H_{c2}) materials than the binary compounds and alloys. As a result of intense research activity during the past decade, many METS compounds have been isolated, their crystal structures determined and their superconducting properties investigated (Table I).³⁻²² As can be seen, high T_c superconductivity is observed in several ternary borides, carbides, silicides, phosphides, oxides and chalcogenides. From the studies carried out on these METS compounds a wealth of information and interesting physics and chemistry have come about not only with respect to the superconducting behaviour but also the coexistence of magnetic order and superconductivity, reentrant behaviour, intermediate valence, heavy Fermion behaviour and mixed (electronic and ionic) conduction. The unique superconducting and magnetic behaviour of the ternary compounds must necessarily arise due to their detailed crystal structures and stoichiometries in a fundamental way.

In the following Sections we shall reiterate the available guidelines and crystal structure-property correlations established for the METS superconductors and

TABLE I

Structure and T_c of known high temperature ternary superconductors

Compound	Structure Type	Latt. Param. (Å)	T_c , K	Reference
LuRh ₄ B ₄	CeCo ₄ B ₄ (tetra)	$a = 5.3, c = 7.4$	11.7	Matthias <i>et al.</i> ⁶
Y(Rh _{0.88} Ru _{0.12}) ₄ B ₄	LuRu ₄ B ₄ (tetra)	$a = 7.5; c = 14.9$	9.6	Johnston ⁷
LuRuB ₂	LuRuB ₂ (ortho)	$a = 5.8, b = 5.2, c = 6.3$	10.0	Ku and Shelton ⁸
Mo ₃ Al ₂ C	β-Mn (cubic)	$a = 6.9$	10.0	Johnston <i>et al.</i> ⁹
Mo ₂ BC	Mo ₂ BC (ortho)	$a = c = 3.1, b = 17.4$	7.0	Toth ¹⁰
Sc ₂ Rh ₄ Si ₁₀	Sc ₂ Co ₄ Si ₁₀ (tetra)	$a = 12.3, c = 4.0$	8.5	Braun and Segre ¹¹
Y ₃ Os ₄ Ge ₁₀	Sc ₂ Co ₄ Si ₁₀ (tetra)	$a = 13.0; c = 4.3$	8.7	Braun and Segre ¹¹
YbRh _{1.4} Sn _{4.4}	Pr ₃ Rh ₄ Sn ₁₃ (cubic)	$a = 9.7$	8.6	Remeika <i>et al.</i> ^{11a}
ZrRuP	Fe ₃ P (hexag)	$a = 6.4, c = 3.8$	13.0	Barz <i>et al.</i> ¹² Muller <i>et al.</i> ¹³
NbPS	NbPS (ortho)	$a = 3.4, b = 11.9; c = 4.7$	12.5	Donohue and Bierstedt ¹⁴
LaRu ₄ P ₁₃	LaFe ₄ P ₁₃ (cubic)	$a = 8.1$	7.2	Meisner ¹⁵
LiTi ₂ O ₄	MgAl ₂ O ₄ (spinel)	$a = 8.4$	13.7	Johnston ¹⁶
BaPb _{0.8} Bi _{0.2} O ₃	CaTiO ₃ (perovskite)	$a \sim 5.2$	13.2	Sleight <i>et al.</i> ¹⁷
Zr _{0.6} Rh _{0.3} O _{0.1}	Fe ₃ W ₃ C (cubic)	$a = 12.4$	11.8	Matthias <i>et al.</i> ¹⁸
Pb _{0.8} Mo _{0.8} S _{7.8}	PbMo _{0.8} S ₈ (rhombo-hexag Chevrel phase)	$a = 9.2, c = 11.48$	15.2	Chevrel <i>et al.</i> ¹⁹ Matthias <i>et al.</i> ²⁰
Cu _{1.8} Mo _{0.8} S ₈	PbMo _{0.8} S ₈	$a = 9.58, c = 10.25$	10.8	Matthias <i>et al.</i> ²⁰
Mo _{0.8} Se _{1.2}	Mo _{0.8} Se ₈ (rhombo-hexag)	$a = 9.64, c = 10.44$	14.0	Sergent <i>et al.</i> ²¹ Perrin <i>et al.</i> ²²

structural instabilities exhibited by them. This is followed by a brief discussion of the structural features of the well-studied METS superconductors and the interesting and exotic phenomena exhibited by them. The data are condensed in the form of figures and tables and elaborate discussions are avoided. For a detailed discussion of the METS superconductors the reader is referred to the reviews and books²³⁻²⁸

EMPIRICAL GUIDELINES AND STRUCTURE-PROPERTY CORRELATIONS

According to the McMillan-Allen-Dynes formalism of the original BCS theory on the origin of superconductivity in a metal T_c is directly dependent on the density of electronic states at the Fermi level, the electron-phonon interaction and phonon density of states, the latter being proportional to the Debye temperature. It is not easy to quantify the above parameters (which govern the T_c) in the absence of detailed information on the crystal structure, electronic band structure and low temperature physical properties for a given system.

Matthias²⁹ and Vandenberg and Matthias³⁰ and Vandenberg³¹ have enunciated a few guidelines for the prediction of superconductivity in binary and ternary systems. These guidelines have been developed empirically but with qualitative theoretical support and successfully applied for the realization of many binary and ternary high T_c superconductors. The T_c of a material is found to be a sensitive function of the crystal symmetry, atomic order and/or stoichiometry, metal atom clustering, lattice instabilities and atomic properties such as average valence electron concentration. Clustering of the metal and/or non-metal atoms is an important feature of the high T_c ternary superconductors. That is, the existence, in the crystal lattice, of metal and/or non metal atom pairs, triangular, tetrahedral or octahedral clusters with short *intracluster* distances (of the same order of magnitude or less than in the parent metal; e.g., PbMo_6S_8 with Mo_6 clusters; LuRh_4B_4 with tetrahedral Rh_4 clusters and B_2 pairs). In addition, the existence of relatively short *intercluster* distances (≤ 20 per cent of the intracluster) is an essential feature since this will ensure conduction band formation and metallic nature of the material while the metal atom clusters ensure the existence of large density of states at the Fermi level. Furthermore, high T_c superconductivity is encountered in systems containing 'isolated' clusters of metal atoms in the crystal lattice. Whenever, there is a 'condensation' or 'fusion' of clusters (by corner, edge or face sharing, e.g., as in $\text{Ag}_4\text{Mo}_9\text{Se}_{11}$, TlMo_3S_3 , LaRu_4B_4), the T_c gets lowered. The important structural features and crystal chemical relationships of METS superconductors are summarized and presented in Table II^{31a}

In binary superconductors, it is well known that certain crystal structures are favourable to high T_c superconductivity (e.g., cubic β -tungsten (A_3B), α -Mn, NaCl and Pu_2C_3 structures). In ternaries, no such favoured structures have yet been found, probably due to lack of sufficient data but generally it is found that high crystal symmetry (cubic, tetragonal, hexagonal or rhombohedral) combined with a 3D-network structure favours high T_c (e.g., PbMo_6S_8 . rhombohedral, LuRh_4B_4

Property	Chevrel Phases LnMo_6Ch_8	Borides		Stannides LnM_2Sn_4 (M = Rh; Os) [$\text{Ln}_3\text{Rh}_4\text{Sn}_{12}$ (I) Sn_4 (II)]	ZrRuP(As)
		LnRh_4B_4	LnRuB_4		
Crystal Structure ^a	Rhombohedral-hexagonal ($a \sim 9.0\text{\AA}$, $c \sim 11.5\text{\AA}$)	Tetragonal ($a \sim 5.3\text{\AA}$, $c \sim 7.4\text{\AA}$)	Orthorhombic ($a \sim 5.8\text{\AA}$, $b \sim 5.3\text{\AA}$, $c \sim 6.3\text{\AA}$)	Cubic or distorted cubic ($a_0 \sim 9.7\text{\AA}$ or $\sqrt{2} a_0$)	Hexagonal (Fe_2P type) ($a \sim 6.5\text{\AA}$, $c \sim 3.8\text{\AA}$)
Metal atom clusters ^b	Octahedral Mo_6 clusters	Tetrahedral Rh_4 clusters	Zig-zag chain clusters of Lu	Pairs (Sn_2)	Triangular clusters of Ru
Rare earth atoms or ions ^c	Large concn ($\sim 7\text{ at\%}$)	Large concn ($\sim 11\text{ at\%}$)	Large concn ($\sim 25\text{ at\%}$)	Large concn ($\sim 15\text{ at\%}$)	—
Role of third element (anion) ^d	S or Se ions	B_2 pairs	B_2 dimers exist which form zig-zag chains	Sn atoms at the site II	P or As ions
Supercond Trans Temp ^e	Arises from Mo-4d band ($T_c \sim 1\text{--}12\text{ K}$)	Arises from Rh-4d band (5-12 K)	Arises from Ru-4d band ($\sim 3\text{--}10\text{ K}$)	Most certainly from [Sn-(5s, 5p)] (1-9 K)	Arises from Ru-4d band (13 K)
Mag ord temp ^f	Low T_m (0.5-1.0 K)	Reasonable T_m (1-12 K)	Low T_m (1-2 K)	Reasonable T_m (1-11 K)	—

^aThe crystal lattice is a truly 3D network structure. The phases are isostructural for a given ternary but lattice constants vary with the Ln or A atom or non-metal.

^bThe intracluster (or pair) distances are very small ($\sim 2.5\text{--}3.0\text{\AA}$, same order as in the respective metals) and the intercluster distances are not very large. This leads to strong metal-metal bonding and also conduction band formation.

^cLn forms part of the crystal lattice and hence is distributed uniformly but isolated effectively ($\text{Ln-M dist} \geq 4\text{\AA}$) from the conduction electrons. Also 4f electrons support a large magnetic moment.

^dThe third element aids in the stabilisation of the structure and has the major role of an anion. Detailed structural analysis and Mossbauer study have shown that Sn(II) site differs from Sn(I) site. Ln size (atomic or ionic radius) is not critical except for LnRh_4B_4 for the formation of proper phase.

^eThe Mo, Ru and Rh 4d conduction bands are narrow. T_c can be high (10-15 K) for nonmagnetic Ln (La, Yb, Lu or Y) or other elements (e.g. A = Pb, Sn or Ca).

^fMagnetic ordering can be ferromagnetic or antiferromagnetic and is exclusively due to the Ln-ion or atom. No superconductivity is observed at any temperature, when T_m is $> 5\text{ K}$ in borides and stannides.

tetragonal; ZrRuP . hexagonal) On the other hand, by trial and error, it has been established that certain crystal structures are *not* favourable to high T_c superconductivity. Examples are · Rare earth ternary rhodium borides and silicides, LnRh_3X_2 ($X = \text{B}$ or Si) with the undistorted hexagonal structures,³²⁻³⁴ and borides with the perovskite structure, LnRh_3B ,³⁵ ternary phosphides and silicides with the orthorhombic TiNiSi or Co_2P or anti PbCl_2 structure, $\text{MM}'\text{X}$ ($X = \text{P}$ or Si ; $M =$ transition or rare earth metal and $M' =$ transition metal)^{13,13a} and ternary silicides MM_2Si_2 with the tetragonal (ThCr_2Si_2) structure.^{36,37}

Yvon⁵ pointed out an interesting feature of the high T_c ternary superconductors in that for those systems which do not possess cubic symmetry, the crystallographic c/a axial ratios fall usually close to 'special' values such as 2, $\frac{1}{2}$, $\frac{1}{3}$, $\sqrt{2}$, $\sqrt{3}/2$ etc. The physical origin of this correlation is not yet clear except that it seems to indicate the influence of Brillouin zone effects and simulation of pseudo-cubic symmetry behaviour.

Another important empirical guideline is the role played by electronic charge transfer effects and the electro-negativity of the non-metallic constituent in inducing high T_c superconductivity in ternary systems This is exemplified by the behaviour of the compounds ZrRuP and ZrRuSi. Both crystallize in the hexagonal Fe_2P structure, which is conducive to high T_c superconductivity. However, while ZrRuP exhibits a T_c of 13 K, ZrRuSi is not superconducting above 1.2 K Since P or Si atoms are isolated in the structure (no P-P or Si-Si bonds exist) it is reasonable to assume that they are present as P^{3-} and Si^{4-} in ZrRuP and ZrRuSi respectively. Since zirconium is always tetravalent there is no effective charge transfer from Zr to Ru in $\text{Zr}^{4+}\text{RuSi}^{4-}$ whereas one electron is contributed to Ru conduction band in $\text{Zr}^{4+}\text{RuP}^{3-}$ Similar arguments can be applied to the isostructural series of compounds NbRuSi, NbRhP, NbReSi, etc where changes in electronic band structure are effected by changes in X and M atoms and where the M' transition metal atoms act as a source or sink of electrons Such empirical considerations have led to the recent discovery of superconductivity in ternary silicides, $\text{MM}'\text{Si}$ ($M = \text{Nb}, \text{Ta}$, $M' = \text{Ru}, \text{Re}$)³⁸

Thus, it appears certain that the existence of isolated transition metal and/or non-metal clusters, and a 3D-network structure with overall simple crystal symmetry give rise to large electron-phonon coupling constants and favourable phonon-density of states and large Debye-temperatures essential for high T_c in METS compounds

SUPERCONDUCTIVITY AND STRUCTURAL INSTABILITIES

Lattice instability is a characteristic feature of many high T_c superconductors e.g., A15 structure compounds, transition metal carbides and nitrides³⁹ In the AMo_6Ch_8 chalcogenides the A atoms, when small, vibrate anharmonically; many of them undergo structural phase transformations (e.g., Cu, Co and Zn-containing compounds) In particular, the compounds exhibiting the highest T_c 's, PbMo_6S_8 and SnMo_6S_8 , have been found to show some structural instability recently⁴⁰

Many of the other high T_c ternary superconductors also tend to be metastable since they compete with other phases of different structure or of slightly different composition. Thus, there are four different modifications of the LuRh_4B_4 borides already known and still more seem likely to exist^{41,42}. In the case of the superconducting stannides $\text{Ln}_3\text{Rh}_4\text{Sn}_{13}$, as many as three different phases of almost the same composition have been reported^{43,44}. A similar situation occurs with some of the superconducting chalcogenides because slight variations of the metal to non-metal atom ratio can produce a series of closely related (isolated or condensed) cluster compounds, such as InMo_6Se_8 , $\text{In}_{\sim 3}\text{Mo}_{15}\text{Se}_{19}$, $\text{In}_2\text{Mo}_{15}\text{Se}_{19}$ and InMo_3Se_3 ^{19,45-47}.

STRUCTURAL ASPECTS OF METS SUPERCONDUCTORS

Ternary Molybdenum Chalcogenides (Chevrel Phases)

The ternary molybdenum chalcogenides $A_x\text{Mo}_6\text{Ch}_8$ (A = Metal, $x = 0.0-4.0$; $\text{Ch} = \text{S}, \text{Se}, \text{Te}$) represent a family of isostructural METS compounds with remarkable chemical and physical properties. Many of them are high T_c (≤ 15 K) and high critical magnetic field ($H_{c2} \sim 600$ kOe) superconductors. Originally discovered in 1971, they have been extensively investigated in recent years. The structure and chemistry of these phases are well understood to a certain extent but a complete understanding of the physical properties including superconductivity, exciting new possibilities and phase equilibrium relationships need a lot more future research. Excellent reviews are available in the literature and hence only a brief account will be presented here.^{2,3,4,23,48-57}

Structure and Stoichiometry—The compounds, $A_x\text{Mo}_6\text{Ch}_8$, possess a hexagonal-rhombohedral crystal structure ($a \sim 6.5 \text{ \AA}$, $\alpha \sim 90^\circ$). The structure essentially consists of a rhombohedral stacking of Mo_6Ch_8 units in such a way that the A atoms occupy the empty channels. Each Mo_6Ch_8 unit consists of an octahedral cluster of Mo-atoms enclosed in a slightly deformed cube of Ch-atoms (Fig. 2). The intracluster and intercluster Mo-Mo distances are small (intra, $2.7 \text{ \AA}$, same as that in Mo-metal, inter, $3.2 \text{ \AA}$) with the result that strong metal-metal bonding exists within the cluster and sufficiently strong interactions exist between intercluster Mo-Mo atoms. The A -atoms are mostly the electropositive elements of the Periodic Table. The stoichiometry x in $A_x\text{Mo}_6\text{Ch}_8$ and the site occupancy depends on the ionic radius of the A metal. Small ionic radius elements (e.g., Cu, Ni, Co etc.) occupy the so called off-channel positions (with essentially tetrahedral coordination of Ch-atoms) and x can vary from 0.0 to 4.0. On the other hand, large ionic radius elements (e.g., Pb, Sn, La, Eu, Yb) occupy the central channel positions (Fig. 2, essentially 8-fold coordination) and x is fixed and close to 1.0. The A -atoms effect an electronic charge transfer to the Mo_6Ch_8 unit (in essence, to the Mo-4d conduction band)^{48,58-60}. Chevrel phases are amenable to a wide variety of chemical substitution at the A , Mo and Ch sites. In addition to $(A_{1-x}A'_x)\text{Mo}_6\text{Ch}_8$ -type solid solutions, isostructural phases $(\text{Mo}_2\text{Re}_4)\text{Se}_8$, $(\text{Mo}_4\text{Ru}_2)\text{Se}_8$, $(\text{Mo}_{6-x}\text{M}_x)\text{Se}_8$, ($M = \text{Nb}, \text{Rh}$), $\text{Mo}_6\text{Ch}_8\text{X}_2$ ($X = \text{Cl}, \text{Br}, \text{I}$), $\text{Cu}_x\text{Mo}_6\text{S}_6\text{I}_2$ and $\text{Li}_2\text{Mo}_6\text{S}_6\text{Br}_2$ have been

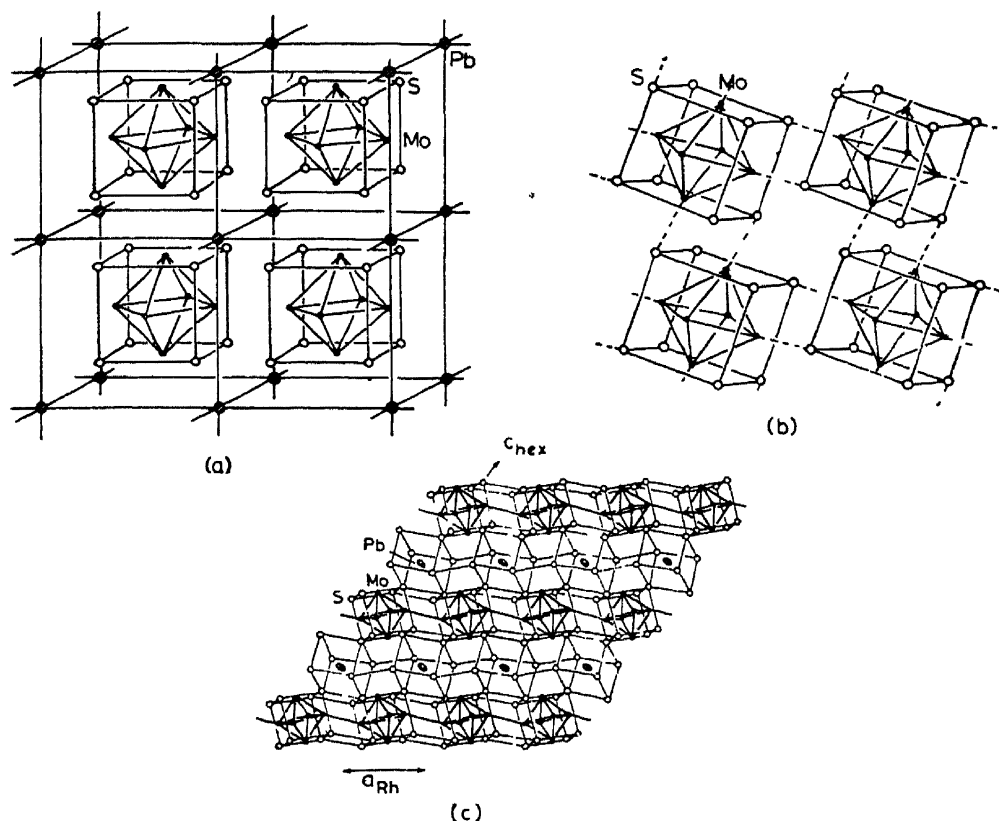


Fig 2 Structure of the Chevrel phases, AMo_6Ch_8 (a) Idealized $PbMo_6S_8$ (b) Mo_6S_8 units showing the distortion with respect to $\bar{3}$ axis and Mo-S bonding (c) Projection along the $(11\bar{2}0)$ plane showing the channels occupied by the Pb-atoms

isolated and studied^{45,46,48,61-67} Interestingly enough, and true to the nature of the channel structure, the A -atoms, when small (e.g., Cu, Co, Ni), can be leached out by a simple mineral acid treatment or electrochemical oxidation to give rise to the binary Mo_6Ch_8 compounds. Of course, the reverse process of insertion of foreign metal atoms into the channels of Mo_6Ch_8 to give ternaries is also possible and has been studied.^{48,49,66,68,69}

Superconductivity and Related Properties—The binary Mo_6Ch_8 and many ternaries, $A_xMo_6Ch_8$ exhibit metallic behaviour, but with fairly high resistivity ($\sim 10^{-3}$ ohm cm). For A = alkali metal, post transition metal or rare earths, the ternaries exhibit superconductivity. T_c values between 8–15 K are encountered for A = Pb, Sn, Cu, Ag, La and Yb. Binary Mo_6Se_8 has a T_c of 6.3 K whereas Mo_6S_8 is superconducting at 1 K and Mo_6Te_8 does not become superconducting upto the lowest temperatures. $Mo_6S_6X_2$ (X = Br and I) exhibit a T_c of 13–14 K. Magnetic susceptibility, heat capacity data and theoretical band structure calculations show that there exists a large density of states at the Fermi level in $A_xMo_6Ch_8$ and the metallic and superconducting behaviour are exclusively due to the Mo-4d electrons^{48,60,70}. The number of electrons per Mo_6 -cluster (NEC) is an important parameter in determining the properties because it determines the occupancy of the

4d-conduction bands For Mo_6S_8 , NEC is 20 $((6 \times 6) - (2 \times 8))$ and it becomes 21, 22 or 23 depending on the valency of *A*-metal in AMo_6S_8 (Ag, $20 + 1$, Pb, $20 + 2$, La, $20 + 3$ etc) but the 4d-conduction band is still partially filled in these cases. Metallic and superconducting behaviour can thus be explained. Band structure calculation and also simple chemical bonding arguments predict that the 4d-sub-band will be completely filled for an NEC of 24 (assuming Mo-Mo intercluster bonding, 12 edges in the Mo_6 -octa cluster require $12 \times 2 = 24$ electrons to form electron-pair bonds) and the material should exhibit semiconductor behaviour (because the upper lying Mo-4d sub-band is separated by an energy of 1.0–1.5 eV). Indeed, the compounds $\text{Mo}_2\text{Re}_4\text{S}_8$, $\text{Mo}_2\text{Re}_4\text{Se}_8$, $\text{Mo}_4\text{Ru}_2\text{Se}_8$ and $\text{Cu}_4^{1+}\text{Mo}_6\text{S}_8$ which possess an NEC of 24 are found to exhibit a semiconductor behaviour.

No universal correlation between T_c and known structural, chemical or physical parameters seems to exist in the Chevrel phases examined so far. A somewhat rough correlation may exist between T_c and hexagonal lattice parameter ratio (c/a) in a related series of compounds but efforts to raise T_c beyond 15 K have not been successful. A detailed explanation for the existence of very large critical fields in Chevrel phases has been provided recently by Decroux and Fischer.⁷¹ The ternary molybdenum chalcogenides exhibit the interesting phenomena of coexistence of superconductivity and magnetic order and also reentrant behaviour. This is discussed in Section devoted to Reentrant Superconductors.

Condensed Molybdenum Cluster Phases—Ternary molybdenum compounds containing $(\text{Mo}_9\text{Ch}_{11})$, $(\text{Mo}_{12}\text{Ch}_{14})$ or $(\text{Mo}_{6/2}\text{Ch}_{6/2})$ ($\text{Ch} = \text{S, Se, Te}$) units resulting from a linear condensation of the octahedral Mo_6 clusters have been recently synthesized and studied. Representative compounds are $\text{Ag}_x\text{Mo}_9\text{Se}_{11}$ ($x \sim 4$),⁷² $\text{A}_2\text{Mo}_9\text{S}_{11}$ ($\text{A} = \text{K, Tl}$), $\text{K}_2\text{Mo}_{15}\text{S}_{19}$, $\text{A}_2\text{Mo}_{15}\text{S}_{19}$ ($\text{A} = \text{K, Ba, Tl}$), $\text{In}_x\text{Mo}_{15}\text{Se}_{19}$ ($x = 2.9\text{--}3.4$),^{19,54} AMo_3S_3 ($\text{A} = \text{K, Rb, Cs}$)⁷³ and AMo_3Ch_3 ($\text{A} = \text{In, Tl, Ch} = \text{Se, Te}$)⁷⁴. The compounds crystallize with a hexagonal symmetry. The a lattice parameter is $\sim 9\text{\AA}$ but the c -parameter varies with the Mo_xCh_y content and decreases to a low value ($\sim 4.5\text{\AA}$) for $x:y = 3:3$. The structure of the $\text{A}_x\text{Mo}_{15}\text{Se}_{19}$ phases is characterized by the presence of Mo_6Se_8 and $\text{Mo}_9\text{Se}_{11}$ units, the latter resulting from a fusion of two Mo_6 octahedra along a common face, but all the Mo atoms have the same chalcogen environment as existing in the Chevrel phases. The intracluster distance is small ($\sim 2.7\text{\AA}$ as in Chevrel phases) but intercluster distance is large ($\sim 3.4\text{--}3.5\text{\AA}$). The indium and other *A*-atoms are situated in a 3D network of channels similar to the $\text{A}_x\text{Mo}_6\text{Ch}_8$ compounds. All the phases examined so far are metallic and superconducting but T_c values are low ($\leq 4.3\text{ K}$) indicating that such structures are not conducive to high T_c .

Ternary Borides with the Stoichiometry AM_4B_4

The four structure types exhibited by the AM_4B_4 compounds (viz., primitive tetragonal CeCo_4B_4 and NdCo_4B_4 -types, bct LuRu_4B_4 -type and orthorhombic LuRh_4B_4 -type) can be described by an arrangement of transition metal tetrahedra, isolated *A* atoms (including the rare earths) and pairs of boron atoms. The CeCo_4B_4 , LuRu_4B_4 and LuRh_4B_4 structure-types are inter-related and all of them contain

more or less isolated M_4 tetrahedral clusters while in the NdCo_4B_4 -type, the M_4 -clusters are fused together by sharing edges such that infinite chains are formed along the crystallographic a -direction

In the ARh_4B_4 compounds with the CeCo_4B_4 -structure, the A -atoms and Rh_4 -clusters (slightly elongated with two short and four long Rh-Rh distances along the tetragonal a and c -axes respectively) occupy the positions of a slightly distorted NaCl lattice (Fig 3). Two orientations of Rh_4 tetrahedra occur and the Rh network can be viewed as forming sheets in the a - b plane (quasi two-dimensional extended clusters) with an alternate arrangement (stacking) of tetrahedra of different orientations along the c -axis. The intracuster Rh-Rh distances (2.6–2.8 Å) are approximately the same as in rhodium metal (2.69 Å) but intercluster distances are large (3.1 Å). The B - B distances are small (1.80–1.83 Å) indicating pair formation whereas the A - A distances are large (~ 5 Å) showing negligible interaction between them. However, significant bonding (charge transfer) exists between Rh and B atoms

The bct (LuRu_4B_4 -type) and orthorhombic (LuRh_4B_4 -type) phases differ from the CeCo_4B_4 -type in the relative disposition of the isolated M_4 clusters in the lattice; whereas the M_4 tetrahedra of the same orientation are joined into sheets perpendicular to the c -axis in the CeCo_4B_4 -type, the M_4 tetrahedra of different orientations are distributed equally in each plane in an ordered fashion in the LuRu_4B_4 and LuRh_4B_4 -type (Fig 3)^{7,41,75}. Thus, the bct and orthorhombic structures can be viewed as containing two interpenetrating three-dimensional networks or extended

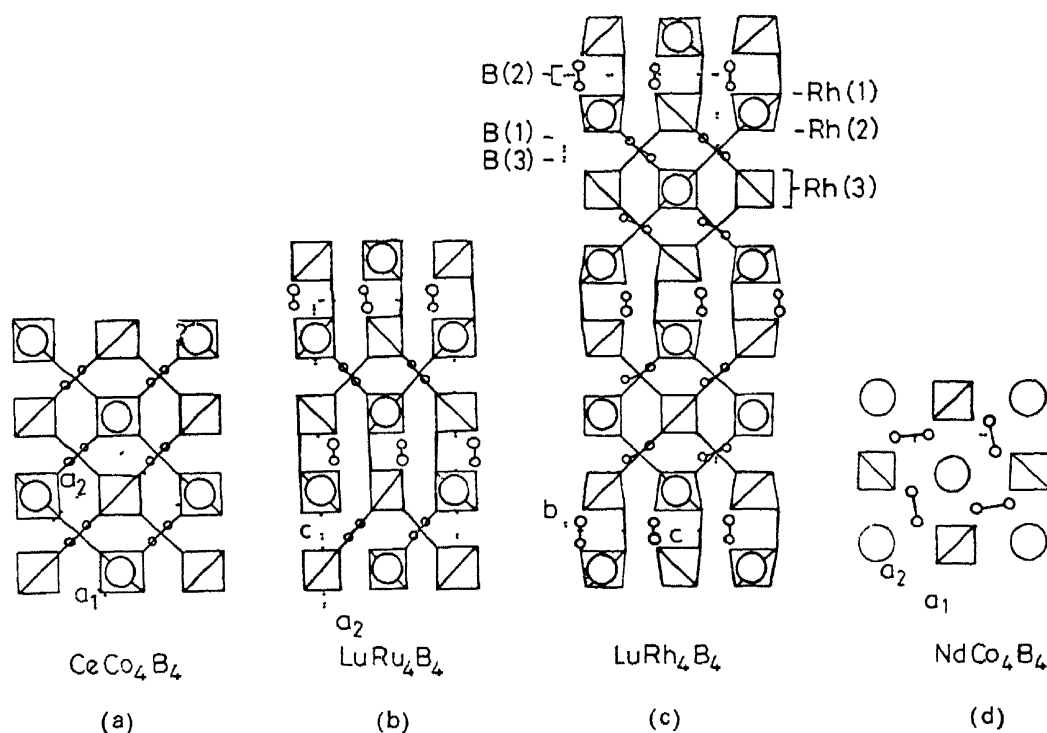


FIG 3 The structure of LuRh_4B_4 (c) compared with those of the other known AM_4B_4 polytypes⁴¹

clusters of M_4 tetrahedra. These extended clusters are qualitatively different from those in $CeCo_4B_4$ -type AM_4B_4 compounds, since in the latter phases they are quasi two-dimensional and do not interpenetrate. However, the unit cell dimensions of the three structures bear simple relationships to each other: $\sqrt{2} a \approx c$ ($CeCo_4B_4$ -type) $\approx a \approx (c/2)$ ($LuRu_4B_4$ -type) $\approx a \approx (b/3) \approx c$ ($LuRh_4B_4$ -type).

The $NbCo_4B_4$ -type structure differs from the $CeCo_4B_4$ -type in two ways, viz., the M_4 clusters are not isolated from each other but are fused together by sharing edges such that infinite chains are formed along the c -axis. Also the $A-A$ distances are small ($\sim 3.8 \text{ \AA} \approx c$ -lattice parameter) so that they can be considered to form infinite linear chains along the tetragonal axis (Fig. 3). On the other hand, the A atoms in the $CeCo_4B_4$ -structure are well separated from each other and form nearly fcc array in the primitive tetragonal structure. The differences between the $CeCo_4B_4$ and $NdCo_4B_4$ -structure types from a topological view point is also brought out by the fact that the c/a ratio is ~ 1.4 in the former while it is much smaller (~ 0.53) in the latter. These structural differences play a crucial role in the T_c behaviour of the compounds.

The formation and stability of the AM_4B_4 compounds with different types of structure are dependent on the relative ionic sizes of the A and M atoms, valence electron concentration and electronic factors. Thus, the proper phase with the $CeCo_4B_4$ -type structure is formed only for the following combinations of elements: $M = Co$, $A(Ln) = Ce$, $Gd \rightarrow Tm$, Lu , $M = Rh$, $A = Nd$, Sm , $Gd \rightarrow Tm$, Lu , Y and Th , $M = Ir$, $Ln = Ho$, Er and Tm . The bct - $LuRu_4B_4$ -structure easily forms for $M = Ru$ and $A = Sc$, Y , Th , U and Ln with the only exception when $Ln = La$. For $M = Os$, only UOs_4B_4 has been isolated. We note that the proper phase with the $LuRu_4B_4$ -structure does not form for $M = Co$ and Rh . However, the structure with $M = Rh$ can be stabilized at the nominal AM_4B_4 stoichiometry by substitution with a few atom per cent of Ru . Orthorhombic $LuRh_4B_4$ -type compounds are known only for $M = Rh$ and $Ln = Ho \rightarrow Lu$. The $NdCo_4B_4$ -type structure is adopted for the following combinations: $M = Co$, $Ln = La$, Nd , Sm , Eu , $M = Ru$, $Ln = La$, $M = Os$, $Ln = La \rightarrow Eu$, Th , $M = Ir$, $Ln = La \rightarrow Dy$, Y and Th . Pseudo-ternary isostructural solid solutions easily form for isoelectronic M elements ($M = Ru$ and Os or Rh and Ir) but, interestingly enough, solid solutions are also found to form for the combinations $Os_{1-x}Ir_x$ and $Rh_{1-x}Ru_x$ with a given A element.

Superconducting Properties The $LnRh_4B_4$ compounds with the $CeCo_4B_4$ -type structure have been studied extensively with respect to superconductivity and related physical properties. The phases containing non-magnetic rare earths Lu and Y exhibit high T_c values (Table III). For $Ln = Nd$, Sm , Er and Tm which can support a magnetic moment due to the 4f-electrons, superconductivity is retained but with a lower T_c (2.7–9.8 K). However, for $Ln = Gd$, Tb , Dy and Ho , superconductivity is destroyed and the compounds order ferromagnetically with Curie temperatures ranging from 5–12 K. The pure compound $ErRh_4B_4$ exhibits a reentrant (metallic) behaviour.³

Solid solutions of the type $(Ln_{1-x}Ln'_xRh_4B_4$ and $Ln(Rh_{1-x}M_x)B_4$ ($M = Ir$ and Ru) have been examined in detail in the literature and provided a wealth of

TABLE III

T_c data on some representative AM_4B_4 compounds^a

CeCo ₄ B ₄ -type		<i>bct</i> -LuRu ₄ B ₄ -type ^b		Orthorh. LuRu ₄ B ₄ -type	
Phase	<i>T_c</i> , K	Phase	<i>T_c</i> , K	Phase	<i>T_c</i> , K
LuRh ₄ B ₄	11.7	Lu(Rh _{0.85} Ru _{0.15}) ₄ B ₄	9.0	LuRh ₄ B ₄	6.2
YRh ₄ B ₄	11.3	Y(Rh _{0.15} Ru _{0.85}) ₄ B ₄	9.4	—	—
ErRh ₄ B ₄	8.7	Er(Rh _{0.85} Ru _{0.15}) ₄ B ₄	7.9	ErRh ₄ B ₄	4.3
TmRh ₄ B ₄	9.8	Tm(Rh _{0.85} Ru _{0.15}) ₄ B ₄	8.3	TmRh ₄ B ₄	5.4

^aTaken from Johnston and Braun.⁴³ Phases with the NdCo₄B₄-type structure do not exhibit superconductivity above 1 K.

^bLuRh₄B₄ and YRu₄B₄ have a *T_c* of 2.0 and 1.4 K respectively.

information on the interplay between superconductivity and magnetism in these materials.^{3,42}

The interesting and unusual properties of the $LnRh_4B_4$ compounds with the CeCo₄B₄-type structure can be explained on the basis of the crystal structure —

(i) The isolated Rh₄ tetrahedral clusters with strong intra and significant intercluster interactions lead to the formation of partially filled conduction bands with a large density of states at the Fermi level (E_F). Hence, the Rh 4*d*-electrons are exclusively responsible for superconductivity and participate in the Cooper pair formation. This has been confirmed by the magnetic susceptibility (χ) and other studies⁷⁶ and band structure calculations.⁶⁰ The Ln -ions have only small but non-trivial effect on *T_c*.

(ii) The rare earth ions exist in 3⁺ oxidation state in the lattice and effect a charge transfer (donation of 3 electrons) to the Rh 4*d*-conduction band. This has been confirmed by $\chi - T$,⁷⁶ Mossbauer⁵² and neutron diffraction.⁷⁷ Because the Ln - Ln separation is large, there is negligible interaction between them and any magnetic ordering due to Ln -ions (which support a magnetic moment) occurs only at low temperatures (≤ 12 K).

(iii) The boron atoms which exist as pairs play the role of anion and stabilize the structure.

The AM_4B_4 phase with the *bct* LuRu₄B₄- or orthorhombic LuRh₄B₄-type structure exhibit a lower *T_c* compared to those possessing the CeCo₄B₄-type structure (Table III). This is due to the differences in the mode of arrangement of the (M_4B_4) tetrahedra of different orientations in the *a-b* plane as well as the stacking of them along the *c*-axis. This can give rise to changes in the density of states at the Fermi level and/or electron-phonon interaction leading to a lower *T_c* in the *bct* and orthorhombic types. However, since isolated clusters exist in all the three structure types, the phases exhibit superconductivity. On the other hand, the NdCo₄B₄-type structure is unfavourable to the occurrence of superconductivity since it

does not contain isolated (M_4B_4) clusters and also, perhaps, because of the small $A-A$ separation

Ternary Phosphides with $MM'X$ Stoichiometry

The fact that a particular structure for a ternary system can favour the high T_c superconductivity is nicely demonstrated by the recent work of Barz *et al*,¹² Muller *et al*,¹³ and Meisner *et al*⁷⁸ on the equiatomic (1 1 1) ternary transition metal phosphides and arsenides of the general formula, $MM'X$ ($M = \text{Ti, Zr, Hf, Nb, Ta}$; $M' = \text{Ru, Rh, Os}$, $X = \text{P, As}$) The compound ZrRuP can crystallize either in a hexagonal ZrRuSi (ordered Fe_2P or ZrNiAl)⁷⁹ type or in the orthorhombic TiNiSi (ordered Co_2P or anti PbCl_2)⁸⁰ type Hexagonal ZrRuP and ZrRuAs show a T_c of 13.0 and 11.7 K (onset temperatures are 13.5 and 11.9 K respectively whereas the orthorhombic ZrRuP exhibits a low T_c of 3.46 K (onset at 3.82 K) Detailed studies are yet to be made on many of the above phases but the available data reveal that the orthorhombic structure is adopted by the compounds with $M = \text{Nb, Ta}$ and the hexagonal arsenide phases are metastable at low temperatures.

An important structural feature of the hexagonal ZrRuP over that of the orthorhombic polymorph is the layered structure of the Zr and Ru atoms (each layer, parallel to the x - y plane and separated by a distance of $c/2$, is occupied by either Zr and P atoms or Ru and P atoms only) and the existence of Ru_3 -triangular clusters (short Ru-Ru distances, 2.63 Å) In contrast, the orthorhombic structure has layers which are filled with Zr and Ru atoms and these layers are all equivalent, also, there do not exist the Ru_3 -clusters¹³ Recent heat capacity data⁸¹ on the superconducting hexagonal phosphides show that the density of states at the Fermi level is not particularly large (0.76 ± 0.15 states/(eV-atom)) for ZrRuP with a T_c of 13.0 K (compare, 1.08 for Ru metal with a T_c of 0.5 K) and hence the high T_c must be due to increased electron-phonon interaction in the ternary system

INTERESTING PHYSICAL PROPERTIES EXHIBITED BY METS SUPERCONDUCTORS

Coexistence of Superconductivity and Magnetic Order

Magnetism and superconductivity are usually considered to be two mutually incompatible phenomena because of the following observations (i) None of the magnetic elements or their alloys are superconducting, (ii) application of sufficiently strong magnetic field ($\geq H_{c2}$) always destroys the superconducting state in a metal and (iii) introduction of even a small concentration of magnetic impurity is very detrimental to superconductivity and can destroy it The latter phenomenon is understood in terms of the well-known magnetic moment-conduction electron exchange interaction Γ Thus, in principle coexistence of both phenomena in a solid can be observed if Γ is small and the magnetic atoms are uniformly distributed in the crystal lattice, Γ can be small if the concentration of atoms is small and also, when they are situated relatively far away from the superconducting electrons. Further, if the coupling of the magnetic dipoles is antiferromagnetic in nature, then there will be no macroscopic magnetic field to compete with super-

conductivity and the realization of an antiferromagnetic superconductor is more likely than a ferromagnetic one where the associated dipolar field is energetically unfavourable for superconductivity.

The discovery of superconductivity in the rare earth containing METS (e.g., LnMo_6Ch_3 and LnRh_4B_4) has brought a completely new situation in the field of solid state science. It is the first time a compound with a magnetic ion present in a regular lattice position, has been found to exhibit superconductivity. All the earlier systems studied were with magnetic ions as doped impurities^{82,83} The immediate interest was to find whether magnetic ordering sets in in these compounds and if so what happens to the superconducting state. Extensive studies have been carried out on these aspects by way of χ , ρ , C_p , H_{c2} , thermal conductivity, thermal expansion, Mossbauer effect and neutron diffraction and it is now established that LnMo_6S_8 with $\text{Ln} = \text{Nd, Gd, Tb, Dy, Er}$ and Yb and LnMo_6Se_8 with $\text{Ln} = \text{Gd, Tb}$ and Er and LnRh_4B_4 with $\text{Ln} = \text{Nd, Sm}$ and Tm exhibit antiferromagnetic order below the respective T_c without destroying the superconductivity in zero applied magnetic fields.^{3,23,25} It is interesting to note that many of the antiferromagnetic superconductors become normal (reentrant behaviour) at T_N and develop some sort of ferromagnetic order by the application of a magnetic field ($H \lesssim H_{c2}$, the critical field)⁵³

The experimentally determined low temperature states (magnetic, superconducting) of 15 distinct ternary phases containing a sublattice of Ln -atoms are summarised in Table IV⁸⁴ The antiferromagnetism exhibited by the ternary systems is exclusively due to the rare-earth ions but the exact type of ordering has been unequivocally established only in few cases. Neutron diffraction measurements⁸⁵ on DyMo_6S_8 revealed that the magnetic structure is characterized by alternating ferromagnetic (100) planes in the nearly cubic Ln -sublattice in which the magnetic moments are parallel or antiparallel to the rhombohedral (111) axis

The anomalous depression of H_{c2} in the vicinity of T_N and other properties of antiferromagnetic superconductors have been recently studied⁸⁶ Several mechanisms by means of which superconductivity is modified by antiferromagnetic order have been considered

Reentrant Superconductors

If the rare-earth spins in the compounds are to order ferromagnetically, the macroscopic dipolar field so created will become strongly competitive with superconductivity and destroy the latter once the critical magnetic field value for the destruction of the superconducting state is reached

Many METS superconductors have been observed to exhibit reentrant superconductive behavior due to the onset of long range ferromagnetic order (Table IV)^{3,52,84,87} The compounds become superconducting at an upper critical temperature T_{c1} and then lose their superconductivity at a second lower critical temperature T_{c2} which is close to the magnetic ordering temperature T_M . The superconducting-to-normal transition at T_{c2} in ErRh_4B_4 is thermal hysteretic⁸⁸ and

TABLE IV

Superconductivity and magnetic order in METS-rare earth (Ln) phases (after Shelton (1983) with modifications)

PHASE	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
$\text{Ln Rh}_4\text{B}_4$	-	S	-	-	-	S/A	S/A	-	F	F	F	F	S/F	S/A	-	S
$\text{Ln Ru}_4\text{B}_4$	S	S	-	N	N	M	N	N	M	M	M	M	M	N	N	S
$\text{Ln Ru}_3\text{B}_2$	-	N	N	N	M	M	M	-	M	M	M	M	M	M	N	N
$\text{Ln Os}_3\text{B}_2$	-	S	S	-	-	-	M	-	M	M	M	M	M	M	N	S
Ln Ru B_2	-	S	-	-	-	-	-	-	-	M	M	M	M	M	-	S
$\text{Ln}_2\text{Fe}_3\text{Si}_5$	S	S	-	-	-	-	A	-	A	A	A	A	A	S/M	A	S
$\text{Ln Ru}_3\text{Si}_2$	-	S	S	N	N	M	M	M	M	M	M	M	M	M	N	S
$\text{Ln}_5\text{Ir}_4\text{Si}_{10}$	S	S	-	-	-	-	-	-	-	-	M	M	M	M	-	S
$\text{Ln}_3\text{Os}_4\text{Ge}_{13}$	-	S	-	M	M	M	N	M	M	M	M	M	M	M	M	S
$\text{Ln}_3\text{Rh}_4\text{Sn}_{13}(\text{I})$	-	-	S	N	N	N	N	M	M	-	-	-	-	-	S	-
$\text{Ln}_3\text{Rh}_4\text{Sn}_{13}(\text{II,III})$	S	S	-	-	-	-	-	-	-	M	M	M	S/F	S	-	S
$\text{Ln}_3\text{Os}_4\text{Sn}_{13}(\text{III})$	-	-	-	-	-	-	-	-	M	S	M	S	S/F	S/F	-	-
$\text{Ln Fe}_4\text{P}_{12}$	-	-	S	A	M	M	N	F	-	-	-	-	-	-	-	-
$\text{Ln Mo}_6\text{S}_8$	S	S	S	A	S	S	S	N	S/A	S/A	S/A	S/F	S/A	S	S	S
$\text{Ln Mo}_6\text{Se}_8$	S	S	S	F	S	S	S	N	S/A	S/A	S	S	S/A	S	S	S

S supercond, A antiferro, M, magnetic, F, ferro, N, neither S nor M

there is a spikeshaped feature in the heat capacity at T_{c2} indicating a first order transition⁸⁹ For HoMo_6S_8 , T_{c1} and T_{c2} are 1.82 and 0.6 K respectively. The spin structure of HoMo_6S_8 is similar to DyMo_6S_8 with Ho^{3+} moments (9.06 compared to the free ion value of 10.0 μ_B) aligned parallel along the rhombohedral (111) direction. Careful neutron scattering studies on HoMo_6S_8 have shown that an oscillatory magnetic state (with characteristic wavelength $230 \pm 50 \text{ \AA}$) coexists with the superconducting state in a very narrow temperature interval around T_M ^{90,91} Coexistence of ferromagnetism and superconductivity has been demonstrated recently in *bct*-type $\text{ErRh}_4\text{B}_3 \square_{0.2}$ ($\square$, vacancy)⁹²

Heavy Fermion Superconductors

One of the interesting recent developments is the observation of superconductivity in a cerium containing METS compound, CeCu_2Si_2 ^{93,94} The Ce 4f electron in this material is responsible for superconductivity and it is proposed that the compound is a 'Kondo-lattice' heavy Fermion system where the charge carriers exhibit large effective masses ($\sim 100\text{--}200m_e$). The heavy Fermion superconductors are characterized by relatively low values of T_c (CeCu_2Si_2 , $T_c = 0.5 \text{ K}$, UBe_{13} , $T_c = 0.9 \text{ K}$, UPt_3 , $T_c = 0.5 \text{ K}$), large values of electronic specific heat coefficient γ — (1000 mJ/mole-K²), large discontinuity in the specific heat at T_c , and large value of H_{c2} and its initial slope, indicating the high thermodynamic stability of this state

It has been suggested that CeCu_2Si_2 and related f-electron systems (UBe_{13} and UPt_3)⁹⁵⁻⁹⁷ may represent examples exhibiting triplet paired or *p*-wave superconductivity^{98,99} while the singlet (spin) paired state (BCS mechanism) is still favoured by some workers^{100,101}. It must be said that no conclusive proof for the *p*-wave superconductivity is as yet forthcoming.

SUMMARY AND CONCLUSIONS

As a result of intense research activity during the past decade, more than 10 classes of METS superconductors, many with $T_c > 10$ K, have been discovered. Efforts have been mainly concentrated on *Ln*-containing systems to study and understand the interplay between magnetism and superconductivity. In this process, new phenomena like heavy Fermion superconductivity (CeCu_2Si_2) and exotic materials (ErRh_4B_4 and ErRh_4B_3)¹⁰² which exhibit reentrant behaviour and coexistence of itinerant ferromagnetism and superconductivity respectively) have been discovered. Experiment has always been ahead of theory in the area of METS superconductors.

Since T_c is a subtle property dependent on various factors like band structure, phonon density of states, electron-phonon interaction etc., it may not lend itself to a simple correlation with atomic or any structure-dependent property in METS superconductors, because the latter are not simple systems. Thus, Matthias rules, so very successful for binary superconductors, have not been useful for ternaries. However, the essential features of the known high T_c METS superconductors viz., the existence of isolated metal and/or non-metal atom clusters, 3D-network structure combined with cubic or pseudo-cubic symmetry are sufficient guidelines in the search for new high T_c compounds. Structural instabilities and metastable nature of the phases, common in binaries, also appear to be a feature of the METS superconductors. Only a few of the large number of known METS have been examined in detail till to-date. Thus, a detailed and systematic study of even the simplest METS of the type $MM'X$ ($X = \text{non-metal}$) is a worthwhile undertaking in the elucidation of structure-superconductivity relationships.

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MATERIALS FOR SAUR VIDDYUT KOSH (SOLAR CHARGEABLE BATTERY)

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The principle of solar chargeable battery (*Saur Vidyut Kosh*) is discussed. The area of research required for development is briefly touched upon. A detailed survey of materials used for developing a photoelectrode is given. Main emphasis is given on new phosphide, chalcogenide and oxide semiconductors. A survey on solar chargeable battery is also made.

Key Words . *Saur Vidyut Kosh*, Solar Chargeable Battery; Photoelectrode; Phosphide, Chalcogenide and Oxide Semiconductors

INTRODUCTION

THE development of any civilization depends upon the available energy resources and in particular, the present civilization is largely dependent upon its fossil fuels like coal, oil, gas, natural uranium and thorium (for India). Scientists have been working round the clock to utilise these fossil materials judiciously to extend the availability of the fossil fuels to the human civilization for the longest possible period. Extinction of such fossil sources is not too far away. The Arab world's threat to shut oil wells in 1972, made us realize what would happen if oil wells were emptied. To overcome the energy problem, new forms of energy are being visualised specially those which are renewable i.e., energy produced at a rate equivalent to the rate of consumption.

Scientists of Ancient India knew how to use solar energy¹ and the product derived out of solar energy to meet their energy demand. Scientists of today have realised that the existence of Man on this planet depends mainly upon his ingenuity to convert solar energy into a useful form of energy. Honda and Fujishima² proved electrolysis of water by solar energy by extending the concept of photovoltaic solar cell to a wet type solar cell (known as photoelectrochemical cell). This cell converts solar energy into electricity or into a chemical form, from which energy could be extracted easily when and where required.³⁻²⁰

A photoelectrochemical solar cell^{7,8} is a special kind of galvanic cell where anode or cathode or both are made of semiconductors. When the semiconductor electrode, dipped into a suitable redox electrolyte, is illuminated with light source of photon energy greater than the band gap of the semiconductor (due to reasons discussed below), photon's energy is converted into electrical energy.

It is necessary to understand the role of semiconductor-electrolyte system to produce electrical energy from photon. A semiconductor has a conduction band which is normally empty of electron and a valence band normally filled with electrons. The maximum energy required to transfer an electron from the highest energy level of valence band (top level) to the bottom level of conduction band is known as the band gap of the semiconductor. The highest valence band's electrons of an extrinsic type semiconductor (*n*-type), however, require very little energy to push them into the conduction band because the Fermi level is about 0.1–0.2 eV below the conduction band. Because of this factor, extrinsic semiconductor becomes a conductor at room temperature. The electrons pushed into the conduction band have the tendency to fall back to the valence band unless there is some force to prevent such process. This opposing force is generated by the help of redox electrolyte in contact with the semiconductor. In order to explain the role of redox electrolyte, it is important to realize that like semiconductor, electrolytes (e.g., $\text{Fe}^{2+}/\text{Fe}^{3+}$, $\text{Ce}^{3+}/\text{Ce}^{4+}$, etc.) also have oxidation levels (equivalent to conduction band) and reduction levels (equivalent to valence band).

The energy necessary to transfer an electron from the reduced species (reduction level) to the oxidised species (oxidation level) is analogous to the band gap of a semiconductor, while redox potential is the potential required to transfer an electron from redox species to the reference level (which is hydrogen scale, NHE), in electrochemistry or zero vacuum level in semiconductor physics or vice-versa. The two reference levels are related as given in eq. 1 —

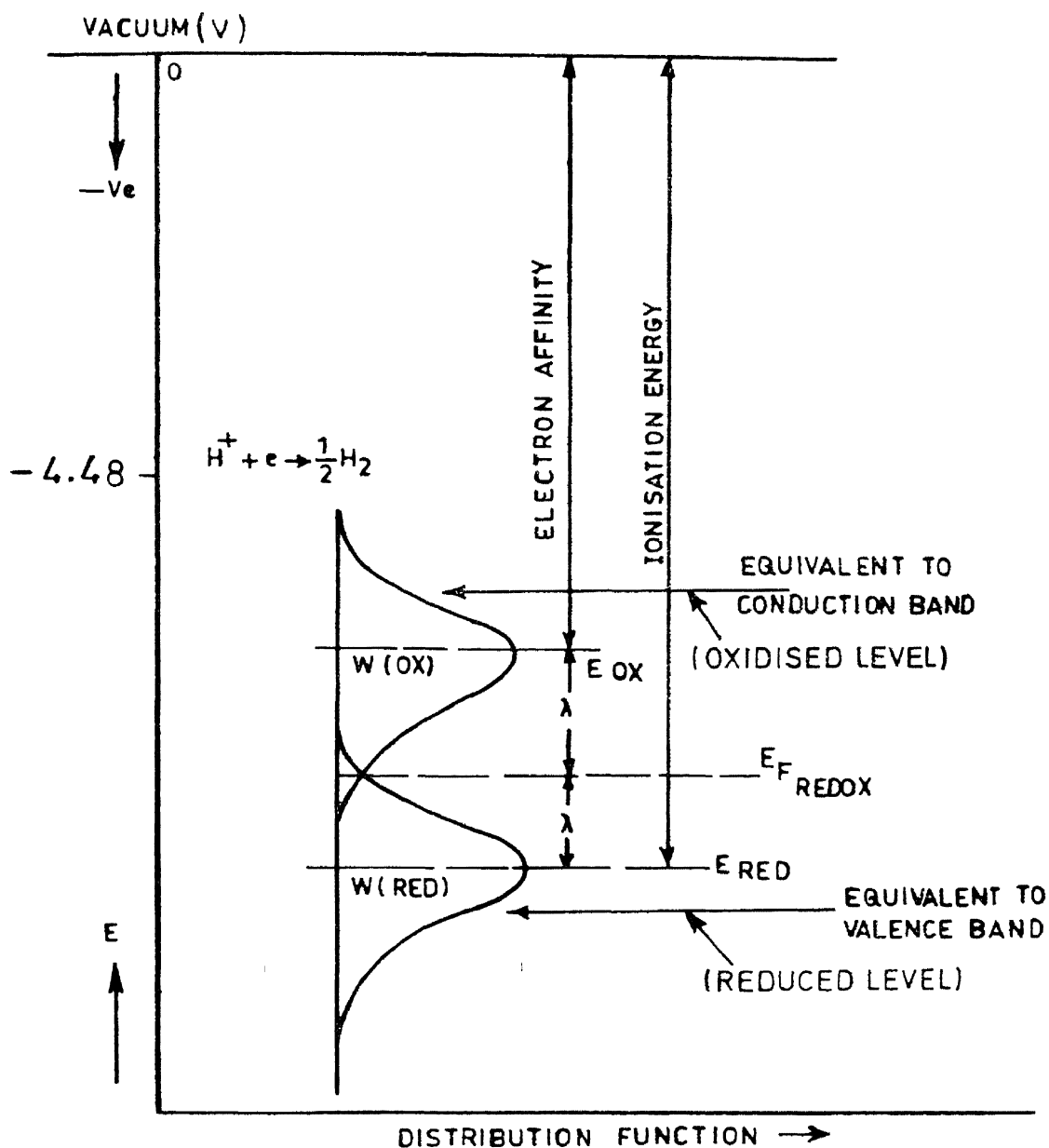
$$E_{\text{vac level}} = (E_{\text{NHE}} - 4.5 \text{ eV}) \quad \dots (1)$$

The electron transfer reaction with redox electrolyte is complicated, because the hydration energy for reduced and oxidised species may not be the same. The difference in energy states of the reduced and oxidised levels can be written as,

$$E_{\text{ox}} + \lambda_{\text{red}} = E_{\text{red}} - \lambda_{\text{ox}} = -E_{F_{\text{redox}}}, \quad (2)$$

where E_{red} is ionization energy for the reduced species (i.e. reduction level), E_{ox} is the electron affinity of the oxidised species (i.e. oxidation level), λ_{ox} and λ_{red} are the polarization or reorientation energy of oxidised and reduced species respectively. The E_{ox} and E_{red} are not discrete, but are broadened into a thermal distribution of states due to (i) thermal fluctuations (ii) interaction with solvent and (iii) interaction with directly bonded ligands. These distributions are shown in Fig. 1, and their distribution is based on Frank-Condon principle.

When a semiconductor comes in contact with a redox electrolyte, the nature of charge transfer at the interface of semiconductor-redox electrolyte would depend upon the nature of level of redox electrolyte overlapping with nature of level of semiconductor. For example, valence band can be acceptor of holes or donor of electrons. It will thus donate electrons to electrolyte, if E_{ox} level overlap with E_v (Fig. 2d). Similarly, the conduction band can accept electrons if E_{red} level overlaps with E_c (Fig. 2c). No effective charge transfer can thus occur if there is no such

FIG 1 Redox energy level and their distribution function (W)

overlaps of two sets of energy levels. Likewise semiconductor can donate its electron to the electrolyte when E_c overlaps with E_{ox} level (Fig 2a) and E_v can accept electrons if E_v overlaps with E_{red} level (Fig. 2b)

When a p -type semiconductor like $\alpha = Fe_2O_3$ doped with nickel (Fig 3a) is brought under a contact with electrolyte (Fig 3b), whose E_{red} nearly overlaps with the valence band, transfer of electrons from the redox electrolyte would occur towards the valence band. This causes the valence band to be populated with energetic electrons (migrated from redox electrolyte) resulting in upward bending of bands as shown in Fig. 3c. The charge transfer reaction makes the surface of the semiconductor positively charged (i.e. populated with holes) and inner side of the semiconductor negatively charged (i.e. populated with electrons). Normally, the charge

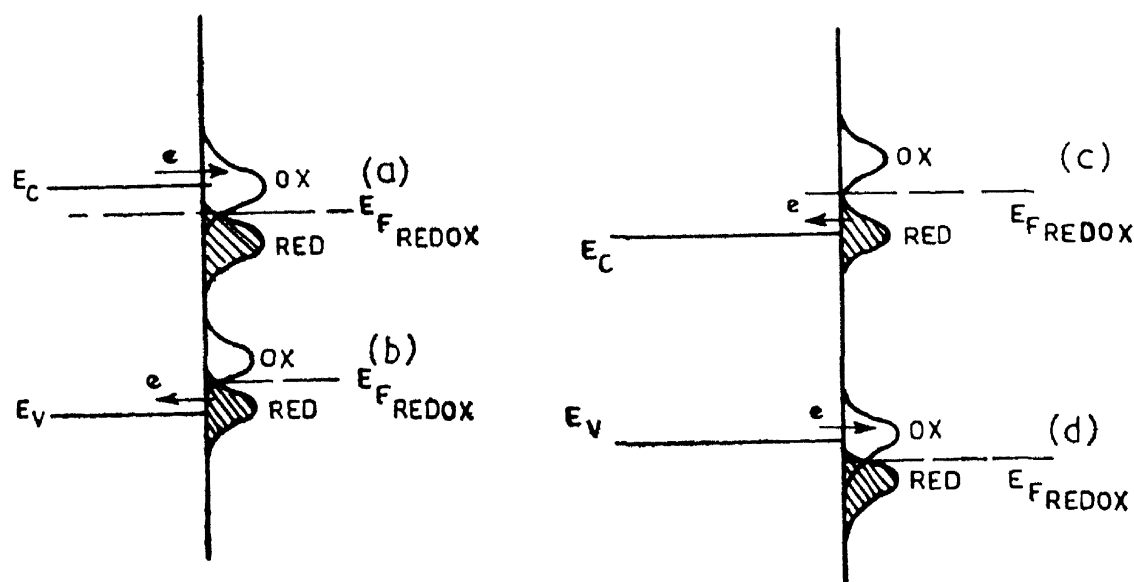


FIG 2 Electron transfer with redox electrolyte

- (a) Oxidation level overlapping with E_C
- (b) Reduction level overlapping with E_V
- (c) Reduction level overlapping with E_C
- (d) Oxidation level overlapping with E_V

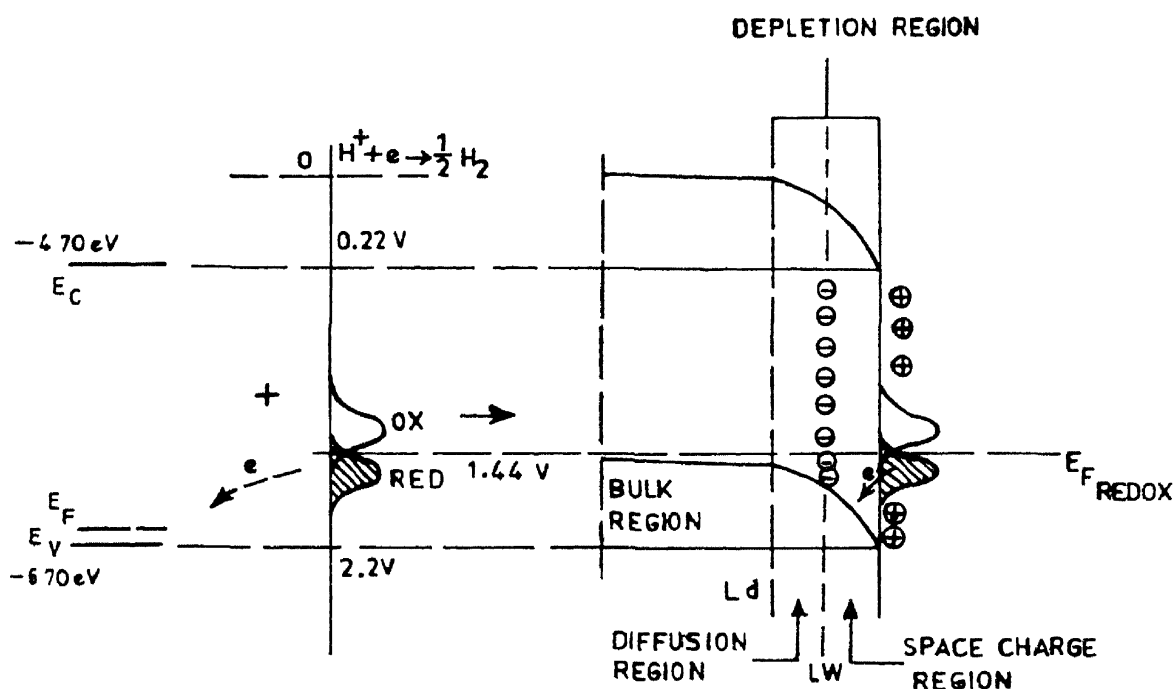
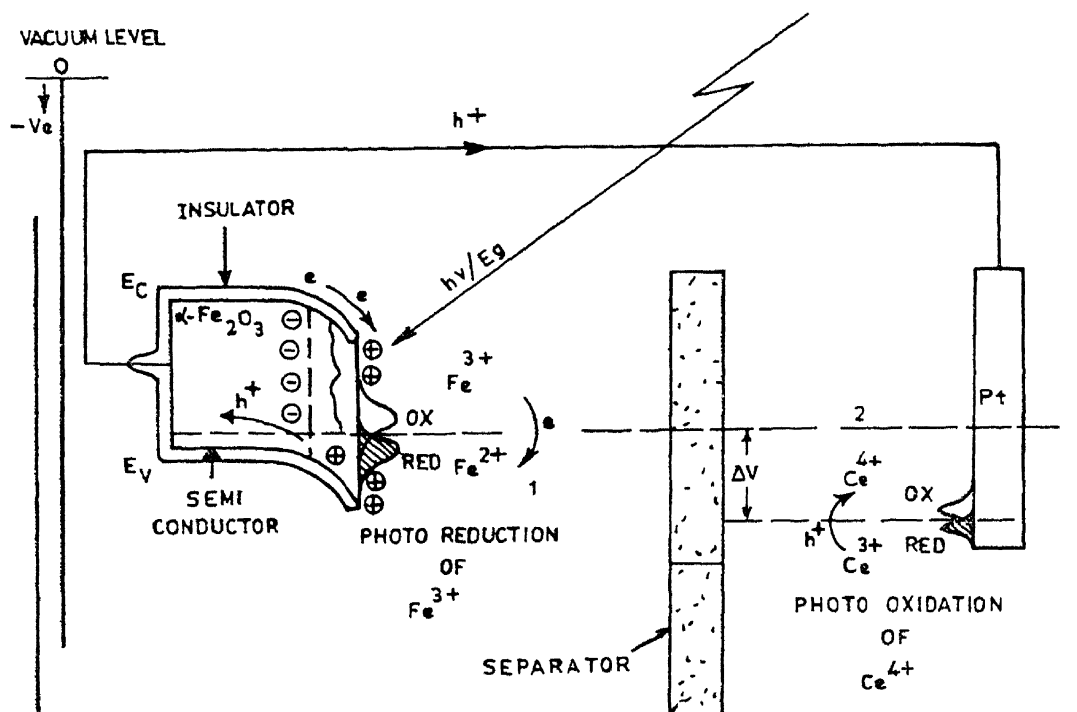
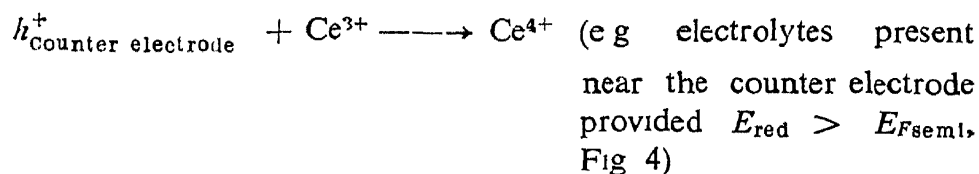
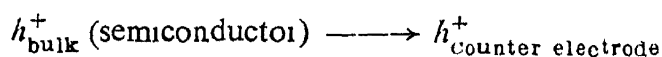
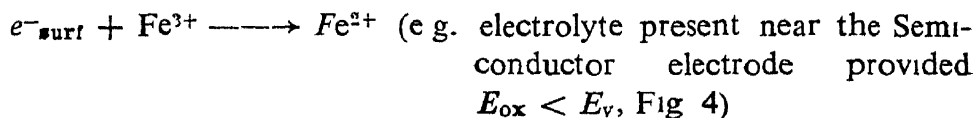
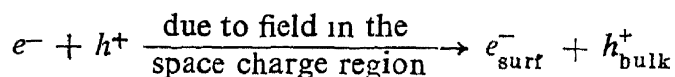
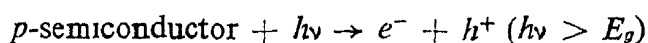


FIG 3 Energy positions of $\alpha\text{-Fe}_2\text{O}_3$ with a redox electrolyte of $E_{F\text{ REDOX}} = 1.44\text{ V}$, NHE (Ce^{+3} , Ce^{+4})

distribution due to this electron transfer within the semiconductor does not occur in one plane (i.e. in plane parallel to the surface), however, for the purpose of understanding and mathematical calculations it is assumed that the electrons which have migrated from the electrolyte to the semiconductor are situated in one plane at a

distance of about 3000 Å from the surface (Fig 3c L_w) The region between this plane and the surface of the semiconductor is known as space charge region. In order to complete the story of charge transfer process, there is also a diffusion region (Fig 3b, L_d) where the concentration of electrons is lower than the space charge region, but greater than the equilibrium concentration of electrons in the semiconductor and a bulk region where the concentration of electrons remains nearly equilibrium. The depletion type junction is at the interface (Fig. 3c). The difference in the valence band of semiconductor and the E_{red} of electrolyte approximately equals the contact potential (ϕ_0). More precisely, one uses the term Fermi level of the semiconductor rather than E_c and E_v and the Fermi level gives an idea of maximum energy the carrier in the semiconductor has achieved either because of doping and/or due to the thermal excitation. For p -type, the Fermi level is near E_v and for n -type semiconductor it is near E_c . The difference in E_c (or E_v) with the Fermi level, E_F , depends largely on the amount of doping. Normally, it is about 0.1–0.2 eV different from E_c (or E_v) as the case may be. For extrinsic semiconductor, thus Fermi level gives an idea of majority carriers, which is electron for n -type and hole for p -type. Similarly, instead of using E_{ox} or E_{red} , for redox electrolyte, one uses E_F redox which is given by eq 2. Thus the difference of E_F (semiconductor) and $E_{F, redox}$ is equal to the contact potential. However, sometime this contact potential is different to the experimentally determined value due to the pinning of Fermi level²²

If the junction near the p -type semiconductor-electrolyte interface is radiated from the electrolyte's surface with photon of energy greater than the band gap of the semiconductor, electrons from the valence band would be excited to conduction band. The electron (minority carrier) of the conduction band will find itself at the surface of the semiconductor due to direction of the field present in the space charge region (Fig. 4). The photogenerated hole (majority carrier) would migrate towards the bulk. The electrolytes present near the surface, can accept the photogenerated electrons provided the E_{ox} level of the electrolyte is below the conduction band of the semiconductor (Fig 4). This electron would reduce the electrolyte present in contact with the semiconductor. The hole will move from the bulk *via* the external circuit to the counter electrode dipped in the same electrolyte where the hole can oxidise the electrolyte. One can get power from this system if, in the external circuit, a resistance is connected in series. This type of cell is known as photo-electrochemical cell. Alternatively, if two electrodes of the cell separated by a suitable membrane²³ containing two different types of redox electrolytes present in two compartment (Fig 4), and the semiconductor is radiated with the photon of energy greater than the band gap, the photogenerated minority carrier would reduce the electrolyte at p -type semiconductor provided E_{ox_1} is below E_c and oxidation of other redox electrolyte would occur at the counter electrode, provided E_{red_2} is above E_F of counter electrode. In the absence of any resistance in the external circuit, the photon energy is converted to chemical energy equivalent to the difference in the redox potentials of two redox electrolytes (i.e., $E_{ox_1} - E_{red_2}$). The photoreactions occurring at the two electrodes can be written as follows:

FIG 4 *Saur Vidyut Kosh* (solar chargeable battery)

net photo reaction is

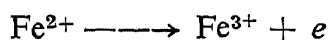


The ΔV in this case is the difference in the redox potential of $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{Ce}^{4+}/\text{Ce}^{3+}$ which is 0.62V. Thus photon's energy is converted to generate ΔV potential in the cell.

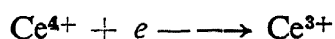
In the absence of photon and under short circuit condition there would be a tendency by the cell, to reverse the reaction by releasing an energy equivalent to 0.62V (i.e. ΔV). If the external circuit is connected in series with a resistance in dark

mode, it will produce power. Thus we have produced a battery²¹ which can be charged by photon energy and discharged in absence of light to get power. However, due to formation of barrier at the junction of semiconductor-electrolyte interface (Fig. 4), there would be a tendency to oppose the dark reaction due to the nature of barrier formed at the surface (depletion region). It is therefore, necessary to use a third inert electrode in the compartment No. 1 to allow the flow of electron from compartment 1 to compartment 2 to carry out following dark reactions.—

A. At the inert electrode of compartment 1



B. At inert electrode of compartment 2



Net reaction being—



—could again be the reactants for photo-reaction process.³

The dark reaction (discharging) would occur between these two inert electrodes, while charging would be done with semiconductor and the counter electrode (Fig. 5). Such a battery is known as the three-electrode system

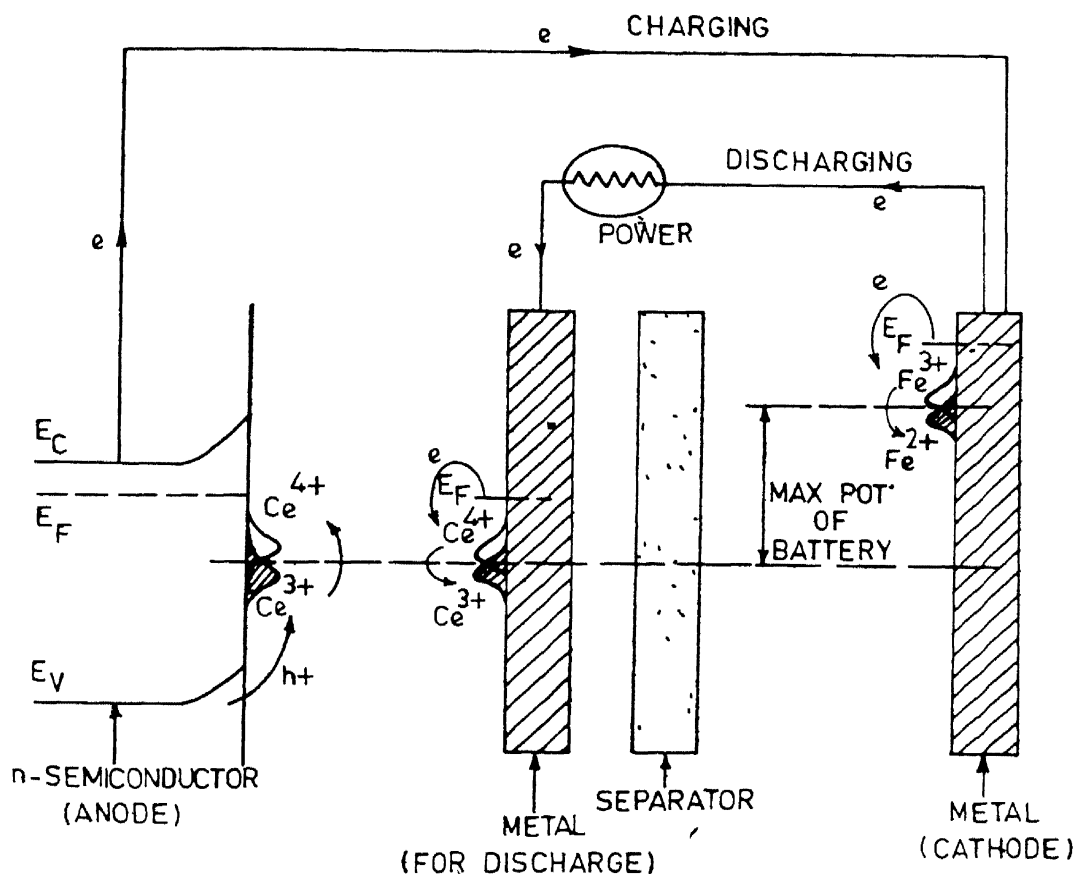


FIG 5 Three electrode storage system.

In order to complete the story of storage battery, it is also possible to replace the counter electrode of compartment 2 with a semiconductor. This semiconductor will have to be n -type (because in compartment 1, p -type has been used) and its energy level should match as shown in Fig 6. Under this condition one additional inert electrode will have to be used in compartment 2, so that dark current could be drawn between the two inert electrodes of compartments 1 and 2. Charging of the battery could be done by illuminating two semiconductors of two compartments simultaneously. At p -type electrode photo-reduction of electrolyte will occur and at n -type, photo-oxidation of electrolyte will occur. The additional semiconductor in compartment 2 is not necessary and it only increases the photon energy conversion efficiency.

If such types of batteries are to be charged with solar radiations, the band gap of semiconductors should be slightly smaller than the photon energy of solar radiations which has the maximum intensity at $AM-1$ (i.e. the intensity of solar radiations measured at sea level with sun perpendicular to the sea level). Considering the theoretical efficiency of semiconductor and spectrum of solar radiation at $AM-1$, the best band gap is found to be between 1.0–1.8 eV with an expected theoretical efficiency of about 30 per cent. Therefore, a battery which is to be charged by solar radiation should have semiconductors of band gap in the region of 1.0–1.8 eV. A battery of type given in Fig 5 and operating with solar energy has been named by our group as *Saur* (the Solar) *Vidhyut* (electricity) *Kosh* (Battery), in honour of

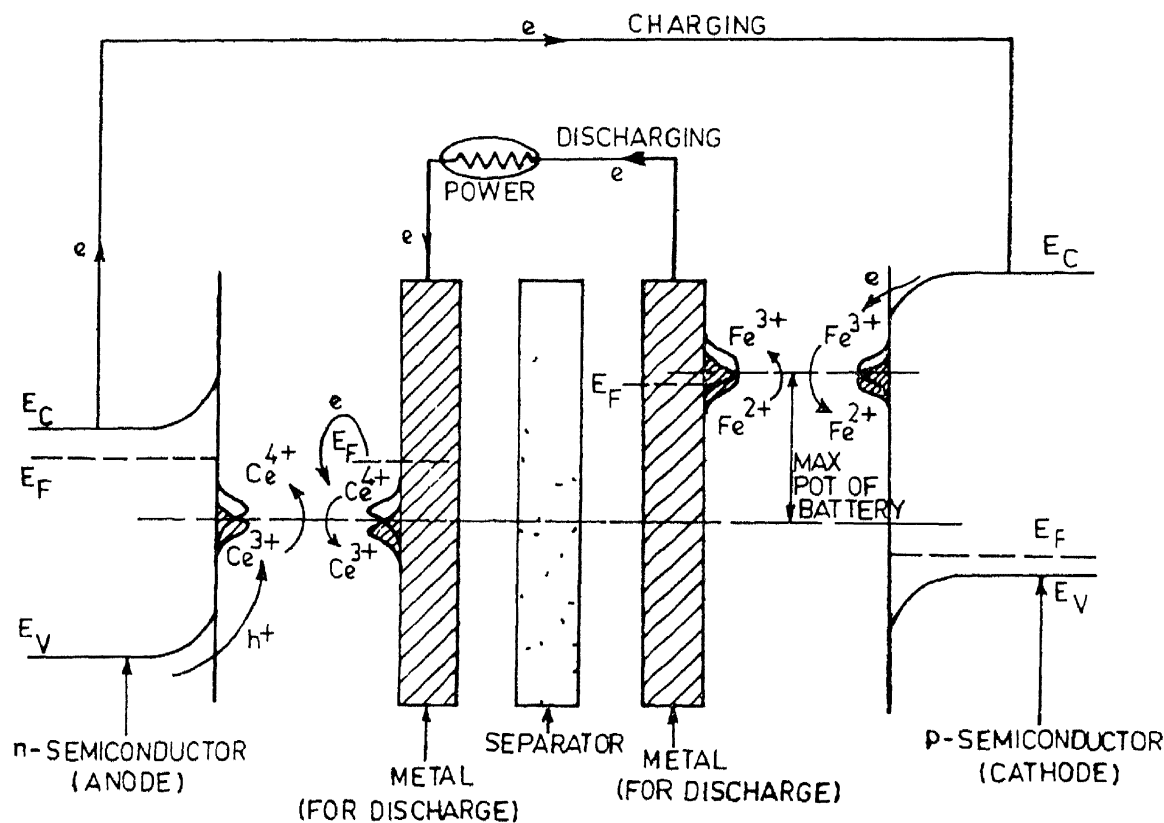


FIG 6 Four electrode storage system

Maharshi Bhardwaj who had given a description of a system to generate power from solar energy

The economical viability of solar chargeable battery depends upon the following factors

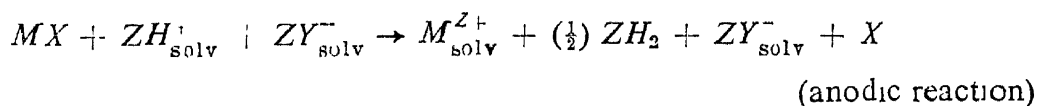
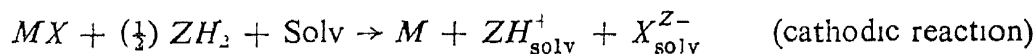
- 1 The efficiency at which the battery is charged by solar energy depends upon the efficiency of converting solar energy into chemical reaction at the interface of the semiconductor-electrolyte. Thus, the photopotential and photocurrent are two important factors responsible for this efficiency
- 2 The efficiency of battery depends upon the current density the battery can retain, the dark potential, the time for which it can retain its charge, and the number of charging/discharging cycles the battery can perform.

The most important issue facing these developments is the development of materials which could efficiently convert solar energy into chemical energy without the semiconductor being chemically and photochemically corroded. Therefore, in the present review, effort is made to review the materials like oxide, chalcogenide and phosphide which have been used to develop photoelectrochemical cell or which could be used for such cell. However, in order to appreciate the photochemical stability it is necessary to learn as to under which condition one could predict the semiconductor to be stable photoelectrochemically. At the end of this review, a list to solar chargeable battery already developed are given in tabular form

PHOTO-CORROSION

The most serious obstacle in the technical use of low band gap semiconductors in contact with aqueous electrolytes is their susceptibility to photodecomposition²⁴⁻²⁶. When the semiconductor electrolyte interface is exposed to photons, the minority carriers (electrons in *p*-type and hole in *n*-type) have two possible ways to react one with the electrolytes present at the interface or with the host material (i.e. with the semiconductor). If these carriers react with the host material, the semiconductor is said to be unstable against photogenerated minority carriers. This can happen in two ways: (i) cathodic decomposition by conduction band electrons (i.e. *p*-type) and (ii) anodic decomposition by valence band holes (i.e. with *n*-type).

The overall energy of corrosion involving holes or electrons are evaluated in such a way that they can be illustrated on the band diagram. Gerischer²⁷ has formulated the expressions for a binary system, *MX* and has considered two reactions



This method has been used to calculate the $n^{E_{\text{dec}}}$ (cathodic decomposition potential) and $p^{E_{\text{dec}}}$ (anodic decomposition potential) of many compounds to

predict the stability of semiconductor against photocorrosion n -type semiconductor would be anodically stable if $p^{E_{dec}}$ is below the valence band-edge of the semiconductor. Similarly p -semiconductor would be cathodically stable if $n^{E_{dec}}$ is above the conduction band-edge of the semiconductor

In order to take advantage of these calculations, especially for new materials, it is also equally important to theoretically calculate the conduction and valence band-edge positions of a semiconductor. The electron affinity values (i.e. bottom of the conduction band) for oxides, chalcogenides or phosphide semiconductors can be calculated by using Butler and Ginley method²⁸. Based upon the bandgap and electron affinity, the valence band position can be calculated. This method can be used for a compound whose chemical formula or empirical formula is known, because both give same result.³

MATERIALS FOR *Saur Vidyut Kosh* (SOLAR CHARGEABLE BATTERY)

We shall now discuss the different classes of materials studied by different schools and summary of results obtained with these materials are shown in respective tables under various classes of materials. However, no effort is made to make any reference for materials having bandgap greater than 2.8 eV, for the reasons discussed earlier.

CHALCOGENIDES

The survey of the chalcogenides which have been studied by different scientists are given in Table I. It appears from this table that chalcogenides of cadmium though has a given efficiency of 10.2 per cent, there is a problem of reproducibility of results. It is thus important to understand why the films prepared by different techniques by different authors give photo efficiency ranging from 0.03–10.2 per cent. There is also a need to find out a system in which it could be stable for at least 1–2 years.

PtS_2 , RuSe_2 ^{104–107}, p -GaSe (2 eV) and n,p -InSe (1.3 eV) have also been recently studied^{108–110}. Chalcogenides of group III-V are also anisotropic, sandwich layer of $X-M-M-X$ being reported to give photoresponse with low dark current in aqueous H_2SO_4 solution¹¹¹. But these three materials though have low bandgap (2.1 eV) they show very low efficiency of 4.5×10^{-4} .¹¹² Recently, a large number of papers have also appeared to understand the electrochemical properties of Mo and W-chalcogenides so that one could understand the reasons for getting variation in the efficiency. Details of observations made with these materials are shown in Table II.

From the survey of materials studied and published by scientists, it appears that tungsten chalcogenide might be the best material for PEC cell. However, this material is not stable for a longer period. There also appears to have inconsistency in the results of different laboratories giving different photo conversion efficiency for same chalcogenides under more or less similar conditions. Thus, there is a need to understand the surface-interface phenomena^{182,183} of the materials as discussed in

TABLE I
Chalcogenide semiconductors

Material	E _g (eV)	Electrolyte System	Flat band Potential (V vs SCE)	Effi- ciency	Electrode form	Quantum efficiency	Voc (V)	Stability	Counter electrode	Refer- ence
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
<i>n</i> -CdS	2.4	NaOH, S, Na ₂ S NaOH, Na ₂ Te NaOH, Na ₂ (SCH ₃ COO) S KCl, K ₄ Fe(CN) ₆ , K ₃ Fe(CN) ₆ NaI, I ₂ in OH ₃ CN	-0.8 to -1.4	0.05 to 9.5	Single crystal thin film poly cryst	8-70	0.4-1.0	Stable in alkaline S/S ⁻² so- lution	C, SnO ₂ Pt,	24,40- 65,67, 68
<i>n</i> -CdSe	1.7	NaOH, Na ₂ S, S NaOH, Na ₂ Se NaOH, Na ₂ Te NaOH, Na ₂ S, S, Se NaOH, Na ₂ (SCH ₃ COO) S, Se Fe(CN) ₆ ^{3-/4-} El ₄ NBFY in CH ₃ O ₄ KOH, Na ₂ S ₂ S _n Fe(CN) ₆ ³⁻ , Fe(CN) ₆ ⁴⁻ , pH > 8 Cesium polysulphides, S, CuSO ₄	-0.9 to -1.45	0.5 to 9.2	„	20-50	0.4-0.77	Stable in NaOH, S ₂ S ²⁻	Pt, C	24,38, 40,42, 45,56- 65,67, 71-74, 5
<i>n</i> -CdTe	1.4	NaOH, Na ₂ Se NaOH, Na ₂ Te K ₂ Se, Se, KOH	-1.45 to -1.50	9.2-10.0	„	51-65	0.70	Stable in K ₂ S ₂ S, KOH	C, Pt	52,67, 68,71
<i>n</i> -CuInS ₂		NaOH-Na ₂ S-S polysulphide	—	3.5- 4.3 0.9	Single crystal Single crystal	—	—	—	—	85,93
<i>n</i> -Re ₂ Se ₃ Cl ₃ 1.42		I ₃ ⁻ , I ⁻ , H ₂ SO ₄	—	—	Single crystal	—	0.49	Stabilised with I ₃ ⁻ /I ⁻	—	95
<i>n</i> -CdIn ₂ Se ₄		KOH-S-Na ₂ S	—	—	Single crystal	—	—	—	—	94

(Continued)

TABLE I (Continued)

Material	Eg (eV)	Electrolyte System	Flat band Potential (V vs SCE)	Effi- ciency	Electrode form	Quantum efficiency	Voc (V)	Stability	Counter electrode	Refer- ence
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
CuIn ₃ S ₈		Sulphide, Polysulphide	—	—	—	—	—	Highly stable	—	103
<i>n</i> -WS ₂	1.3	halide solution	—	6.5	—	—	—	Stabilised in halide solution	—	92
<i>p</i> -WS ₂		CH ₃ CN/(<i>n</i> -Bu ₄ N)ClO ₄	0.8	—	—	—	—	—	—	66
<i>n</i> -MoS ₂	1.7	Et ₄ N, halide ion in CH ₃ CN NaI, I ₂ (aq) Fe ²⁺ , Fe ³⁺	—	0.02–4	,,	1–53	0.03 to 5.0	Stable in Fe ²⁺ , Fe ³⁺	C, Pt	69–71, 75–77
<i>n</i> -MoSe ₂	1.4	I/I ₂ Fe ²⁺ , Fe ³⁺ (Et ₄ N) X, 2 in CH ₃ CN X = halogen KI, I ₂ HBr, Br ₂ , pH=0	+0.5 – +4.4	0.02–9	Single crystal		0.09 to 0.55	Stable in I ₂ , I ⁻ and Fe ²⁺ , Fe ³⁺	Pt	78–87, 75, 24
<i>n</i> -WSe ₂	1.57	Fe(CN) ₆ ^{3+/4+} NaI, I ₃ ⁻ , pH=1 NaI, I ₂ , Na ₂ SO ₄ H ₂ SO ₄ , pH=0	–0.45	14	Single crystal		0.71	Stable in Fe(CN) ₆ ^{3-/4-}	Pt	70, 88, 89
<i>p</i> -WSe ₂	1.35– 1.57	Fe ^{2+/3+} , H ₂ SO ₄	–0.8	2			0.51			81, 90
<i>n</i> -Bi ₂ S ₃		NaOH-Na ₂ S-S		0.14–4.7	Polycryst- alline film (doping na- ture impro- ves effici- ency)	—	0.08 to 0.18			53, 91

TABLE II

Material	Observations	Ref
$n\text{-MoS}_2$	1 Charge transfer is favoured with surface $\parallel C$ more than with surface $\perp C$	96
	2 Cleavage steps and dislocations enhanced the photocorrosion of these material	97
MoSe_2	1 Due to the presence of indirect band gap the observed efficiency is lower than expected theoretical value	96
	2 The pinning of Fermi level is observed to affect the efficiency.	75
	3 Highest output power is observed at low temperature ($< 15^\circ\text{C}$)	98
	4 Stable and efficient cells are demonstrated in polyiodide electrolyte	99,100
WSe	1 High efficiency is observed with polyiodide couple	101
	2 Co-existence of n and p in the same crystal surface leads to carrier recombination	102
	3 Fermi level pinning observed	22

Table II so that the cause of different results obtained by different authors could be understood. The stability of material has to be increased perhaps by modification of surface of the material. Therefore, time has come to probe into these factors, rather than carrying out experiment to produce materials with another technique without increasing the reported efficiency of the material. It is disheartening to read papers explaining a new technique of preparation with efficiency ten times lower than the maximum efficiency already achieved by other authors and not making any effort to study the reason of getting lower efficiency. A valid question also comes to the mind, as to what is the justification for omitting the study of PEC properties with large number of chalcogenides of other elements of periodic table, and concentrating only on elements like Hg, Bi, Cd, In, Ga, Mo, and W. It is quite possible that there might be some other chalcogenides, possessing the requisite properties to make an efficient PEC cell. Therefore, there is a need to screen all possible chalcogenides which could be tried for PEC cell. The criteria for such screening should naturally be as follows —

- (i) Material should have band gap in the region of 1.0–2.6 eV so that solar energy could be used for excitation effectively
- (ii) Technique of preparation of material should be simple and material should be cheap
- (iii) The materials should be chemically and photochemically stable in aqueous solution (either acid or alkaline solution)

Based on these three factors, we have carried out a survey of chalcogenides of all unstudied elements of periodic table and elements which conforms to the above three properties listed in Table III. Amongst all unstudied elements of periodic table it is observed that chalcogenides of As, Sn, Hg and Sb are the only suitable materials meeting the above three requirements.

TABLE III
New chalcogenides

Compound	Band gap (eV)	Method of preparation	Structure	E_g (eV)	Solvent in which soluble
As_2Se_3	1.6	By direct combination of elements at high temperature	rhombohedral, black crystal	4.61	Alkali
As_2Te_3	1.0	„	monoclinic	4.81	—
Bi_2S_3	1.3	By passing H_2S through a solution of Bismuth trioxide	rhombotic group powder	4.6	HNO_3
HgS	2.0	By the action of alkali sulphide on mercuric salts	Hexagonal, brownish black crystals	4.69	Aquaregia
$SnSe_2$	1.2	By melting tin and selenium at $650^\circ C$ in vacuum	dark brown crystals	4.7	Strong HKO_2
$SnSe$	1.2	By melting tin and selenium in exact proportions at bright red hot temperature	rhombic, steel group	4.48	Alkali
SnS	1.08	By passing H_2S to an acidic solution of stannous chloride	rhombic, brown crystal	4.67	Conc HCl
Sb_2S_3	1.7	By direct combination of elements with feeble incandescence	rhombic, yellowish red	4.78	In H_2SO_4
$ZnSe$	2.67	By direct reaction of zinc salt with Potassium selenide	Hexagonal, Pale red	3.92	Acids
$ZnTe$	2.26	By direct combination of element at high temperature.	Cubic, red crystal	3.94	Alkali

7 BAND EDGE POSITIONS OF CHALCOGENIDES (CALCULATED BY BUTLER-GINLEY METHOD)

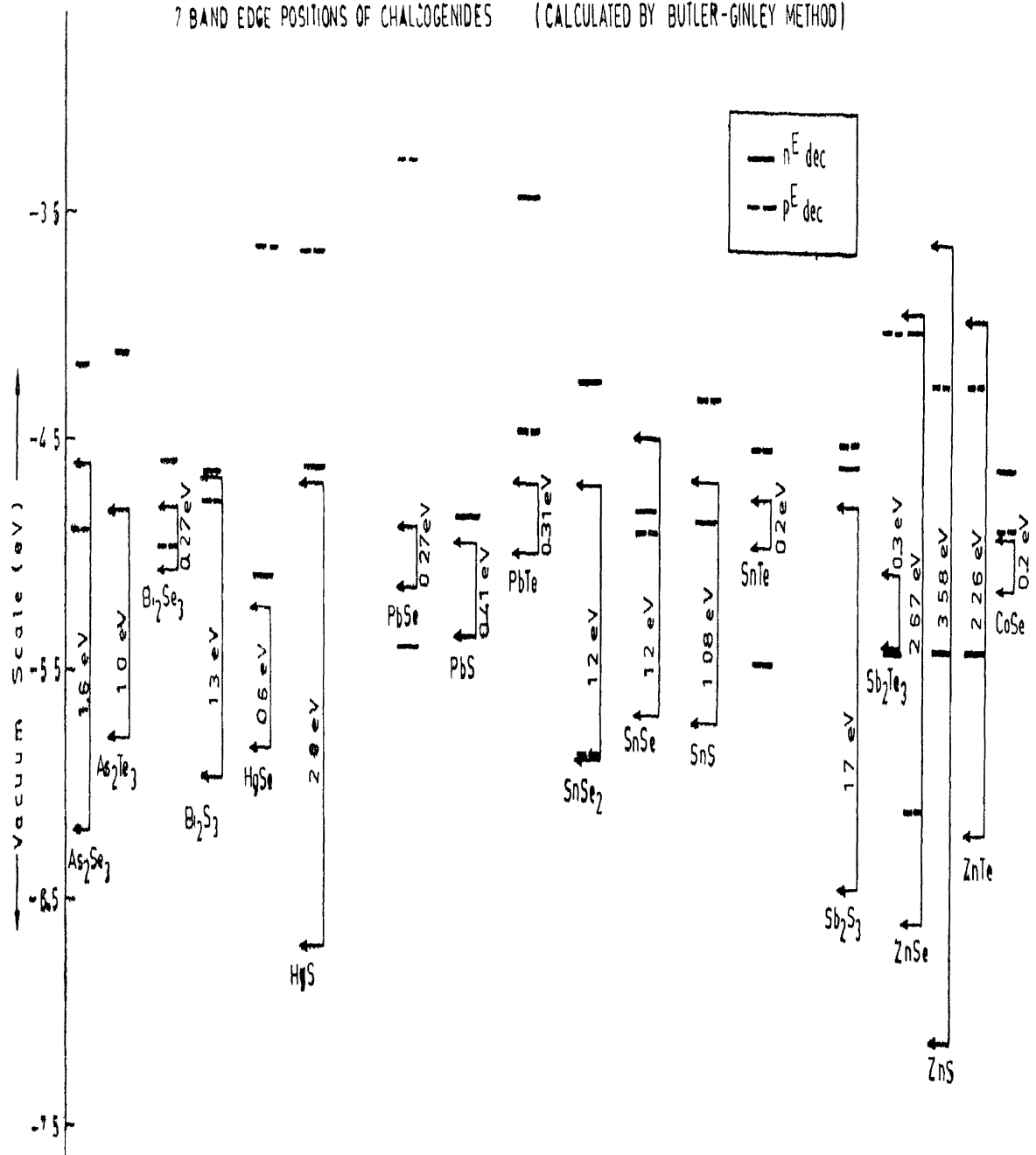


FIG 7

Since most of these materials are unstudied, it is important to predict their stability theoretically and also establish their band diagram. Therefore, anodic and cathodic photocorrosion potentials and the band diagram of these chalcogenides have been calculated⁴ and are shown in Fig. 7.

Based on these calculations it is observed that As_2Se_3 (1.6 eV), As_2Te_3 (1.0 eV), Bi_2S_3 (1.3 eV), HgS (2.0 eV), SnSe_2 (1.2 eV), and Sb_2S_3 (1.7 eV) are cathodically stable, i.e. their cathodic decomposition potentials are less negative to their conduction band-edge value. But none of these materials are found to be anodically stable, i.e. the anodic decomposition potentials are less negative to the valence band-edge of these materials. Other materials like zinc chalcogenides being high bandgap and Bi_2Se_3 , PbSe , PbS , PbTe , SnTe , Sb_2Te_3 and CoSe being low bandgap materials are unsuitable for PEC cell but the former materials may find their application in PEC cell if their bandgap is reduced by making a mixed chalcogenides $\text{MX}_x\text{Y}_{1-x}$, where X may be S or Se and Y may be Te because it has been observed that the bandgap of chalcogenides can be controlled by adding the controlled amount of Te or mixing telluride with other metal chalcogenides.¹¹⁴ The bandgap can be changed from 0 to 2.5 eV by mixing of HgTe with CdTe .

The chalcogenides of unstudied element suggest the necessity to study the electrochemical and photoelectrochemical properties of AsSe_3 , As_2Te_3 , Bi_2S_3 , HgS , SnSe_2 and Sb_2S_3 , so that one may be able to decide the worthiness of these materials for PEC or solar chargeable cells.

PHOSPHIDE SEMICONDUCTORS

The survey of literature on phosphide semiconductors reveals that except InP , GaP , Zn_3P_2 , ZnP_2 , CuP_2 , CdP_2 , no other phosphides have been studied for PEC cell (Table IV). A question again comes to mind as to why phosphides of other elements of periodic table have not been tried for PEC cells? We, therefore, undertook

TABLE IV

Compound	E_g (eV)	Electrode form	Electrolyte	Efficiency	V_{oc} (volts)	I_{sc} (mA cm^{-2})	Ref
$n\text{-InP}$	1.26	single crystal	$\text{NaOH} \text{Fe}(\text{CN})_6^{-4}/^{-3}$ $\text{NaOH-Na}_2\text{Te}$ $\text{VCl}_2\text{-VCl}_3\text{-HCl}$	18.6	Stable for 10 hrs	—	155 188
$P\text{-InP}$	—	single crystal	„	0.4–11.5	0.66	25	156
$n\text{-GaP}$	2.25	single crystal	—	—	—	—	142
$P\text{-GaP}$	—	single crystal	Na_2SO_4 pH 2.5	—	—	—	157–
$P\text{-ZnP}_2$	1.1	single crystal	—	—	—	—	161
CdP_2	2.0	—	—	—	—	—	162
Zn_3P_2	1.32	alkaline EDTA	—	6.1	—	—	163
$P\text{-}\alpha\text{-ZnP}_2$	2.1	alkaline pH = 13 $V_{fb} = 0.7\text{ V}$ (SCE)	—	12.0	—	—	162, 163, 190

to carryout a survey of phosphide materials of all unstudied elements of periodic table meeting the three requirements described earlier. It is observed that the phosphides of alkali and alkaline earth metals are soluble in water giving phosphine gas^{115,116} and thus are not suitable for PEC cells. Phosphides of elements of Gr IIIA and phosphide of metals like Pt, Pd, Au are also not suitable for an economically cheap PEC cell. Therefore, the phosphides of unstudied elements which could be useful for PEC cell, are of elements of Co, Cr, Fe, Mn, Mo, Ti, V, W and Zr because phosphide of these elements are expected to be chemically more stable in aqueous solution. The bandgaps of some of these phosphides are given in Table V. The reported metallic and semiconducting phosphides are given in Table VI.

TABLE V
Bandgaps of some phosphides

Metallic Phosphides and Bandgap < 0.6		Medium Bandgap Phosphides		
Material	Ref	Material	E _g	Ref
CrP ₄	164	AlP	2.50	174
MoP ₄	165	BP	2.2	176
VP ₄	164	CdGeP ₂	1.8	174
CoP ₃	166	Cd ₃ SnP ₂	1.5	174
PdP ₂	167	Ga _{0.85} As _{0.15} P _{1.5}	1.44	113
FeP	168	In _{2/3} PSe ₃	1.55	171
TiP	169	ZnGeP ₂	2.20	174
α -WP ₂	170	ZnSiP ₂	2.20	174
FeP ₂	171	ZnSnP ₂	2.10	174
PtP ₂	167			
FeP	172			
TiP	170			
WP ₄	165			
MnP	173			
VP ₂	170			
ZrP ₂	170			
NiP ₂	167			

TABLE VI
Properties of new transition metal phosphides

Material	Empirical Formula	E _g (eV)	Photocurrent I _{sc} (mA/cm ²)	Electron Affinity (eV)
Cobalt phosphide	CoP _{0.5}	0.89 0.67	0.223	5.02 5.13
Iron phosphide	FeP _{0.7}	0.86	0.919	3.97
Molybdenum phosphide	MoP _{1.0}	0.97 0.67	0.75	4.54 4.60
Nickel phosphide	NiP _{0.41}	0.89 0.65	1.77	4.29 4.40
Vanadium phosphide	VP _{0.63}	0.78	1.26	3.27
Tungsten phosphide	WP _{5.55}	9.93	0.25	4.94

In the absence of available literature on the bandgap of various possible phosphide of these selected elements we decided to prepare the phosphides by a direct combination of metal with phosphoric acid, such that concentration of phosphoric acid is kept in very large excess to metal present in the reaction vessel³ The slurry of metal/phosphoric acid is then heated at different temperatures for different duration of time until all phosphate is converted into phosphide. The dry powder is reduced in hydrogen atmosphere for various duration at different temperatures, until a phosphide is obtained with a bandgap of around 1.0 eV because it is reported that the bandgap can be increased with increase in P content in $\text{GaAs}_{1-x}\text{P}_x$ ($0 < x < 1$)

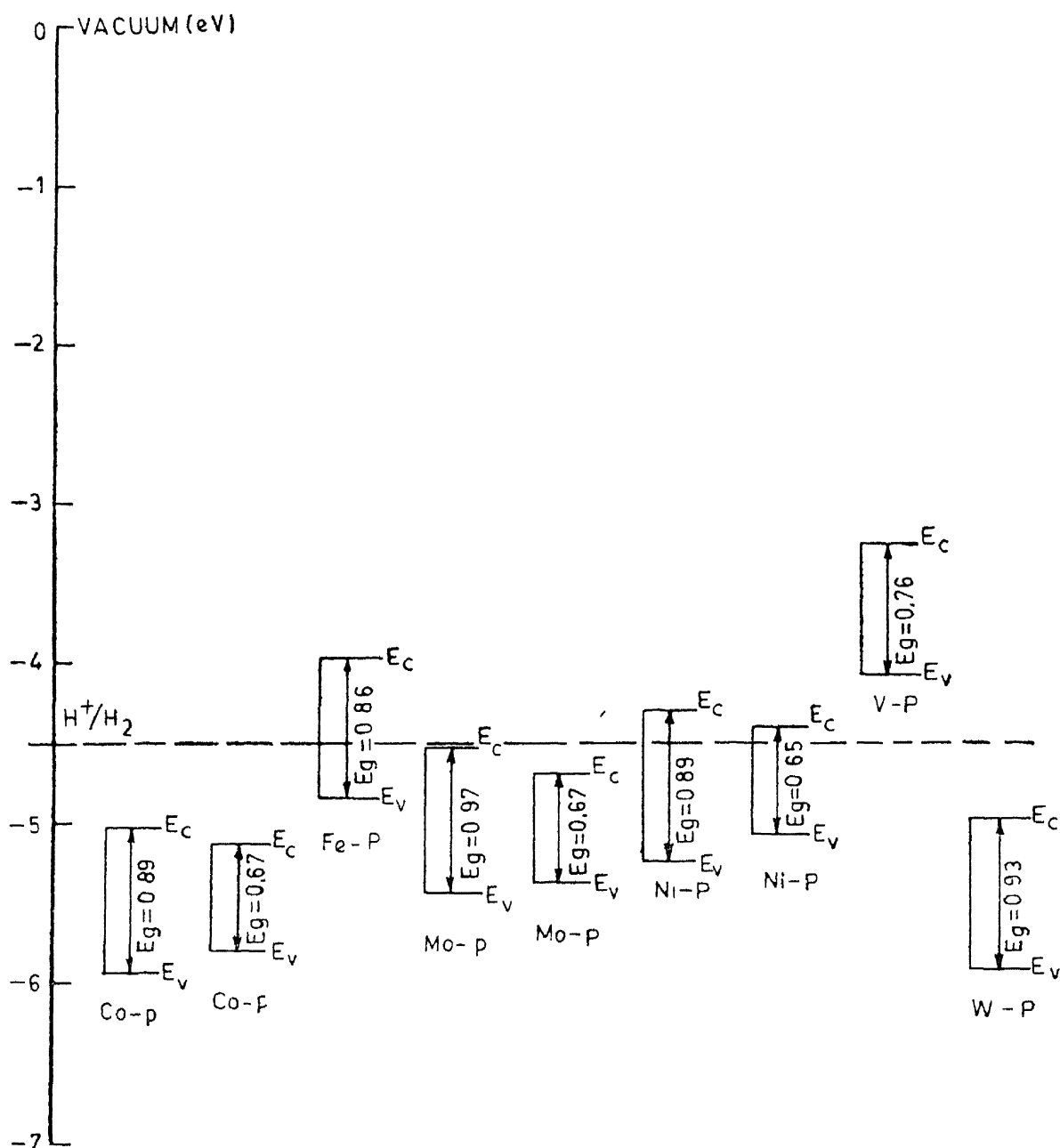


FIG 8 Positions of conduction and valence band-edges

from 1.44 ($x = 0$) to 2.25 ($x = 1$)¹¹⁷. The materials obtained at each of the above treatments were analysed to determine the structure and the bandgap. All materials which could be produced to a composition giving bandgap around 1.0 eV were studied for their photoresponse. The empirical formula of these new materials were determined by EDAX. The conduction and valence band-edges were calculated by Butler-Ginley method.

It was observed that phosphides of Cr, Mn, Ti and Zr could not be prepared of bandgap around 1.0 eV by this method. However, these elements may give lower bandgap by reducing them at temperature higher than 1200 °C. Due to non-availability of high temperature set-up, we could not reduce at temperature greater than 1200 °C. Results of these observations are given in Table VI and the band diagram of these new phosphide materials are shown in Fig. 8.

It is obvious from Table VI that we should make in depth study of phosphides of Co, Fe, Mo, Ni, V and W with a hope that one of them might prove its worth for PEC cell. Our group is actively working on these new phosphide materials. However, amongst published literature, phosphides of In and ZnP_2 seem to be promising materials.

OXIDE SEMICONDUCTORS

Some of the properties of the oxide semiconductors of bandgap below 2.8 eV reported in the literature are shown in Table VII. Amongst the narrow bandgap oxide semiconductors, Fe_2O_3 , Pb_3O_4 , $\text{PbFe}_{12}\text{O}_{19}$, $\text{PbTi}_{1.5}\text{W}_{0.5}\text{O}_{6.5}$, LuRhO_3 and CdIn_2O_4 are few oxides which are found to be stable in electrolytic solution. However, $\alpha\text{-Fe}_2\text{O}_3$ and Pb_3O_4 may be economically viable materials to be explored. The theoretical efficiency of these compounds is expected to be around 20 per cent whereas in laboratory one has been able to get efficiency of about 1 per cent. Therefore, there is a need to understand the reasons for getting low efficiency and effort should be made to achieve the expected efficiency. Both these materials ($\alpha\text{-Fe}_2\text{O}_3$ and Pb_3O_4) are stable in alkaline solution^{30,34}. There is also a need to make a systematic survey of all oxides of cheap metals having band gap in the region of 1.0–1.8 eV. Similarly, there is a need to make a systematic study on mixed oxides like titanates, molybdates and arsenates on lines as made for chalcogenides and phosphides.

MISCELLANEOUS TYPES OF MATERIALS

Materials other than those discussed earlier and which are being studied for PEC cell includes GaAs, Si etc. are given in Table VIII. Amongst these compounds GaAs and CuInS_2 seem to show some promise for their use in a PEC cell. However, none of these is stable for longer duration in the electrolyte.

SOLAR CHARGEABLE BATTERY

Scientists have been trying to fabricate a solar chargeable battery by using a variety of materials and redox electrolytes. The batteries which have been published are

TABLE VII
Oxide semiconductors

Material	E _g (eV)	Flat band potential (V vs SCE)	Efficiency %	Nature of electrode	Stability	Ref.
Fe ₂ O ₃ { E_g 4.71 E_v 5.88}	1.7-2.2	-0.67	0.9	Single crystal	in pH > 8	29,30
WO ₃	2.8	-0.20	—	Single crystal	Stable Unstable under illumination	189 29,31
CdO	2.1	-0.20	—	Polycrystalline	Unstable	32
V ₂ O ₅	2.75	+0.45	—	Polycrystalline	Unstable	33
Bi ₂ O ₃	2.8	-0.32	—	Polycrystalline	Unstable	33
PbO	2.8	-0.54	—	Polycrystalline	Unstable	33
<i>n</i> -Pb ₃ O ₄	2.1	-0.31	0.09	Polycrystalline	—	34
<i>p</i> -CuO	1.7	+0.06	—	Polycrystalline	Unstable	34
(Li doped)	1.35	+0.55	—	Polycrystalline	Unstable	35
FeTiO ₃ { E_g 4.3 E_v 5.72}	2.16	-0.10	—	Single crystal	—	39,140
FeTiO ₃	2.58	-0.60	—	Single crystal	—	36
Fe ₂ TiO ₅	2.18	+0.50	—	Single crystal	—	37,36
YFeO ₃	2.60	-0.46	—	Single crystal	Stable	36,37
Hg ₂ Ta ₂ O ₇	1.80	-0.20	—	Polycrystalline	Unstable (<i>n</i> -type)	32
Hg ₂ Nb ₂ O ₇	1.80	+0.30	—	Polycrystalline	Unstable (<i>n</i> -type)	32
PbFe _{1/2} O ₁₀	2.30	+0.20	—	Single crystal	Stable	32
PbTi _{1/3} W _{2/3} O _{6.5}	2.4	-0.40	—	Polycrystalline	Stable in acid	32
SrTiO ₃	—	—	2.0	Polycrystalline	—	150
CdFe ₂ O ₄	2.3	-0.10	—	Polycrystalline	—	32
LuRhO ₃	2.20	+0.34	—	Single crystal	Stable-hole mobility = 2.5 cm ² /V sec Electron mobility = 1 cm ² /V sec	38,35 118
CdSnO ₄	2.12	±0.1	—	Single crystal	Unstable	39
CdIn ₂ O ₄	2.23	+0.7 ± 0.1	—	Single crystal	Stable	39
<i>p</i> -GeFe ₂ O ₄	2.30	—	—	Single crystal Hall mobility = 2 cm ² /V sec	—	175

TABLE VIII

Material	E _g (eV)	Electrolyte	Efficiency	V _{oc} (Volts)	I _{sc} (mA cm ⁻²)	Electrode	Ref
<i>n</i> -GaAs	1.4	Fe ²⁺ /Fe ³⁺ I ⁻ , I ₃ ⁻ S ²⁻ , S _n ²⁻ Fe(CN) ^{-3/4} Fe ²⁺ /Fe ³⁺ , EDTA KOH, Te ²⁻ , mTe ²⁻	12 with Fe ²⁺ /Fe ³⁺ 3.3 1.5	1.09 0.72 0.47	0.89 11.67 8.33	Si-doped Wafers	38,89, 119-131, 136,137
<i>n</i> -Si	1.1	FeCp ₂ , <i>n</i> -Bu ₄ N, ClO ₄ in ethanol (FeCp ₂ = ferrocene) I ⁻ /I ₃ ⁻ , FeCl ₂ /FeCl ₃	12-5.8	0.3	—	Single crystal	132-135, 138,139, 141-145
<i>p</i> -GaAs	1.4	I ⁻ , I ₃ ⁻ , pH = 0 KCl, VCl ₂ /VCl ₃ E _u ³⁺	0.5-1.3 0.6	0.2 0.3	30	Single crystal	89,146- 149
<i>p</i> -Si	1.1	VCl ₂ -VCl ₃ , HCl	0.06-11.5	0.66	25	Single crystal	151-154 16
GaAs _{0.71} P _{0.29}	—	Non aqueous electrolyte	13	1.01	15.7	—	113

TABLE IX
Solar chargeable batteries

Photo-electrode	Storage voltage (V)	Electrolyte redox species	$I_{\text{photocharge}}$ (mA/cm ²)	Storage electrode	Photo voltage (V)	Counter electrode	$I_{\text{discharge}}$ (mA/cm ²)	Ref
CdSe	—	S ²⁻ /Sn ²⁺	—	Ag ₂ S	—	Pt	—	177
CdSe	—	"	—	"	—	C	—	178
MoSe ₂		Br ⁻ /Br ₂ /I ⁻ /I ₂	200	Pt	0.49	Pt	20.6	86
		HBr/Br ₂ /Nafion/HI/I ₂ pH = 3.5		HI/I ₂ /Pt				179
GaAs	0.50	Se ²⁻ /Se ₂ ²⁻	100	Cd	0.50	Pt	14.6	179
CdSe	0.40	S ²⁻ /Sn ²⁺ /Se ²⁻ /Sn ²⁺	100	Pt	0.40	Pt	0.75	179
CdS		S ²⁻ /Sn ²⁺		Co/Co(ON) ₂		Pt		180
CdSe				Sb/Sb ₂ O ₃				
BaTiO ₃		Fe ²⁺ /Fe ³⁺		Ce ⁴⁺ , Ce ³⁺		Pt		181
n-Pb ₃ O ₄		Fe ²⁺ , Fe ³⁺		IO ₃ ⁻ , I ⁻		Pt		183
n-WSe ₂ or n-MSe ₂		I ⁻ , I ₃ ⁻		AQ(AQH ₂)	1.0	C		185
				(Sodium 9-10 anthra (hydro) quinone 2,6 disulphonate)				184
n-WSe ₂		I ⁻ , I ₃ ⁻		n-InP/S ²⁻ , Sn ²⁺		Cd		184
n-CdSe		Se ²⁻ /Se		p-CdTe/Cd ²⁺				186
P-InP		C ₄₄ H ₄₈ N ₂ Fe ³⁺	20	Nafion/Ru ²⁺ (bpy) ₃	1.3	n-CdS Zn		187 21

shown in Table IX. But none of these has been found economical and therefore, the research is required to find a suitable non-corrosive photoelectrode and storage redox electrolytes. One can use storage electrodes like Ag/AgCl, Cd/CdS, Ag/Ag₂S, where one does not need any separator. However, research is required to confirm their effectiveness in the battery.

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PROTON CONDUCTION IN SOLIDS

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Recent advances in the study of solids with high proton conductivity have been reviewed. Many superionic solids or solid electrolytes have been developed for Ag^+ , Cu^+ , Li^+ , Na^+ , K^+ , F^- , O^{2-} but not many good proton conducting solids are still available. Reasons for this have been identified. Important experimental techniques for studying proton transport have been outlined. Two novel techniques for the study of ion transport used by us are laser Raman and NMR studies under d.c. bias. A general discussion of different transport mechanisms is also presented.

Solid hydrates have been identified as a special group of materials which can sustain high proton conduction. Recent investigations in our laboratory have shown that the interlayer water or water of crystallization of these solid hydrates can be electrolysed which supply the mobile charge carriers.

Applications of solid proton conductors are also reviewed. Special mention has been made of two devices studied in our laboratory, viz. solid state dehumidifier and *in situ* solar energy storage system.

Key Words : Proton Conduction and Conductivity; Superionic Solids; Ion Transport; Laser Raman, IR and NMR Spectra; D.C. Bias; Solar Energy Storage System

INTRODUCTION

THE charge transport in solids takes place *via* (i) electrons (ii) holes and (iii) positive and negative ions. Electrons are the charge carriers in metals. In semiconductors, the conductivity can be due to electrons and/or holes. Alkali and silver halides are the earlier known solids in which conductivity is due to ion motion. Their ionic conductivity was, however, very small ($\sim 10^{-14} - 10^{-16} \text{ ohm}^{-1} \text{ cm}^{-1}$). Recently, a large number of solids discovered show high ionic conductivity. Such solids termed as fast ion conductors or solid electrolyte or superionic solids, conduct monovalent cations (e.g. H^+ , Li^+ , Na^+ , K^+ , Ag^+ , Cu^+) with the exception of anion conductors for O^{2-} and F^- . For high conductivity, the number of charge carriers as well as their mobility should be large. The ion transport may be facilitated by the thermally generated point defects or may be provided by some inherent structural disorder. This review tries to present an overview of the perspectives and problems associated with fast proton transport in solids. The proton conductors are of great use in fuel

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cell, hydrolysis cell, high energy density batteries and charge transport in complex biophysical system. However, no reliable work was started until a few years ago despite many earlier claims of proton conduction in a series of solids.²

MECHANISM OF ION TRANSPORT—PHENOMENOLOGICAL AND STRUCTURAL APPROACH

The ionic solids can broadly be grouped into the following two groups on the basis of their conductivity or defect structure.

- i Point defect type Insulating Ionic Solids, and
- ii Molten Sublattice type Superionic Solids.

The transport mechanism for the two types are entirely different as briefly described below

Transport in Point Defect Type Ionic Solids

The ionic solids belonging to this class (viz., alkali and silver halides) possess conductivities lower than $10^{-10} \text{ ohm}^{-1} \text{ cm}^{-1}$ at room temperature

An ideally perfect ionic crystal would be an insulator if the ion transport under the action of an electric field is assumed to take place via anion-cation exchange only. This process involves a very high energy of $\sim 15\text{eV}$.³ However, all ionic solids are known to have a finite (though small) conductivity. This is attributed to the presence of thermally generated Schottky and Frenkel defects in the lattice. These 'point defect type' ionic solids can be further sub-divided according to the defect concentration as follows.

- (a) Dilute or low concentration

The number of mobile defects is $\leq 10^{18} \text{ cm}^{-3}$

Examples are (alkali and silver halides)

- (b) High concentration

The defect concentration is $> 10^{18} \text{ cm}^{-3}$

These solids behave as fast ion conductors at high temperatures. Examples are (Stabilized Zirconia or Hafnia, CaF_2 etc.)

In general, the electrical conductivity is given by

$$\sigma = \sum_i n_i q_i \mu_i, \quad (1)$$

where, n_i is the number of charge carrier, q_i the charge on the i th ion, and μ_i the mobility of the charge carrier or i th ion

Here, the charge carriers are thermally generated Frenkel or Schottky defect pairs. Their number (n_i) and mobility (and hence the conductivity) are temperature dependent.³ The number of these Frenkel (n_F) and Schottky (n_S) defects are given by the following expressions

$$n_F = (NN')^{1/2} \exp \left(-\frac{g_F}{2KT} \right), \quad (2)$$

and

$$n_S = N \exp \left(-\frac{g_S}{2KT} \right), \quad (3)$$

where g_F and g_S are the energies of formation of Frenkel and Schottky defects. N' is the number of normal lattice sites per unit volume N is the number of interstitial sites per unit volume

The ionic mobility μ_i is given by the expression

$$\mu_i = \frac{a^2 q_i}{KT} \nu_0 \exp \left(-\frac{\Delta G}{KT} \right), \quad \text{..(4)}$$

where ν_0 is the vibrational frequency of the ion around its equilibrium position, ΔG is the energy difference between the saddle point and lattice site position (i.e., energy barrier for the migration of ion)

and a is the interatomic distance.

Hence, the conductivity for materials with Schottky or Frenkel defects is given by

$$\sigma_S = n_S \mu_S q = \frac{Na^2 q^2 \nu_0}{kT} \exp \left(-\frac{g_S/2 + \Delta G_S}{kT} \right) \quad (5)$$

and

$$\sigma_F = n_F \mu_F q = \frac{(NN')^{1/2} a^2 q^2}{kT} \nu_0 \exp \left(-\frac{g_F/2 + \Delta G_F}{kT} \right). \quad (6)$$

It is obvious that a plot between $\log \sigma T$ vs $1/T$ would be linear for both the cases

In the above discussion, we have assumed that all the defect pairs are thermally generated. However, doping can also change the defect concentration (and hence the conductivity). For detailed analysis of doped alkali halides reference may be made to Chandra and Rolfe⁴, Fuller⁵, Friauf⁶ and Chandra¹

The defect concentration, in general, can be altered by aliovalent doping apart from changing the temperature. For most cases the conductivity of ionic conductor is due to both the above reasons. So, 'point defect type' superionic conductors generally show high conductivity only at high temperatures. For example, PbF_2 is a good fluoride ion conductor at high temperatures only because of the increased number of thermally generated Frenkel interstitials⁷. The O^{2-} ion conductors are doped ZrO_2 , HfO_3 , ThO_2 , CeO_2 etc, in which tetravalent cations are partially replaced by di or trivalent impurities (Ca^{++} , Y^{+++} etc).

Transport in Molten Sublattice Type Superionic Solids

A disordered or defect structure provides a situation where mobile ions are possible. One way is to create this by generating point defects thermally or through doping as described above. The other more promising situation is an inherently

disordered structure where the available number of sites in one or both the sublattices are more than the ions, permitting ions to 'hop' almost like a 'free ion' from one site to another. All these ions act as charge carriers. The high mobility or conductivity in this class of solids is further permitted by a 'channelled' or 'layered' structure. The number of mobile ions are $\sim 10^{22} \text{ cm}^{-3}$. The study of fast ion transport in a large number of materials indicates several, more or less, common criteria for high ionic mobility as given below.

(i) *Ionic Radius and Charge*—A small cation or anion is likely to move more freely than a relatively large ion in a lattice. The cations have relatively small ionic radii compared to anions. Therefore, most of the superionic materials developed so far are for monovalent cations like Li^+ (0.60 Å), Na^+ (0.95 Å), K^+ (1.33 Å), Cu^+ (0.96 Å) and Ag^+ (1.13 Å). The anions have large ionic radii, e.g. F^- (1.36 Å) and O^{2-} (1.40 Å) and so anionic conductors are difficult to obtain at low temperatures. Recently, Dunn and Farrington⁸ have reported a few materials showing high mobility at high temperatures for divalent cation Ba^{2+} , Cd^{2+} , Sr^{2+} though it is much less than that for monovalent ions. This is somewhat expected since the coulombic energies involved in jumping/hopping of di-or-trivalent ions are more than that for monovalent ions.

Another related criterion is that the mobile ions should be weakly bound to the rigid lattice. Smaller ions are called upon to be bonded more strongly to the lattice, whereas the small ionic radii would permit greater ease in its movement as discussed earlier. Therefore, in most materials a compromise has to be struck between both these effects which control the net mobility. For example, Li^+ ion in $\text{Li}-\beta$ alumina despite its small ionic radii or size, is much less mobile than Na^+ in $\text{Na}-\beta$ alumina, apparently as a consequence of a weaker Na-O bond.⁹

(ii) *Ionic Polarisability*—Diffusion through the faces of the coordination polyhedron is made easier by the large polarisability of the mobile species as well as that of antagonist ion. The latter possibly distorts its electronic cloud during movement of the mobile ion. Analysis of the electronic properties of various fluorides crystallizing with the same structure shows that larger is the polarisability of the cations, the greater is the ionic conductivity.¹⁰

(iii) *Covalency of rigid lattice*—Ionic mobility would be higher if the bonding energy between the mobile ion and antagonist ion is weak. A good example is LaF_3 which involves three types of fluorine atoms. The more mobile anions have the longest La-F distance.¹¹ Another interesting example is that of ternary compounds of formula $\text{MM}'_m\text{X}_n$, in which the $\text{M}-\text{X}$ bond may be weakened as a consequence of a strengthening in the competing $\text{M}'-\text{X}$ bond. Consequently, in isostructural materials, the optimal mobility is obtained when the rigid lattice is the most covalent possible. Such examples are hollandite type materials.¹²⁻¹⁴

(iv) *Coordination Number of Mobile Species*—Fast ionic mobility is easier for mobile species with low coordination number because a large opening of the 'bottle neck' is provided between the two neighbouring sites. In some Ag^+ and Cu^+ good ionic conductors the mobile cations have coordination numbers 4, 3, 2 in the

equilibrium positions¹⁵ whereas silver is 6-coordinated in poor ionic conductors like AgF, AgCl, AgBr.

Similarly for anionic conductor the lower is the coordination number of anion, the greater is its mobility¹⁰ For example, in NaF, CaF₂ and LaF₃ the fluorine anionic coordinations are 6, 4 and 3 respectively and consequently their conductivities are such that $\sigma_{\text{NaF}} < \sigma_{\text{CaF}_2} < \sigma_{\text{LaF}_3}$

(v) *Structure and Concentration of Mobile Ion*—For a large concentration of mobile ions, the energy difference of the cation-anion interaction in the various sites involved in the conduction mechanism should be small. Further, there must be a sufficient number of vacant sites for an ion to hop/jump. Structure is probably the most important factor responsible for high ionic conduction. Table I gives the structural parameters of some superionic solids. A highly 'disordered structure' is the common factor in all the materials which means that the number of sites in the cationic sublattice is more than the number of cations in the unit cell. Thus the percentage occupancy of each site is low. A free ion like hopping of these ions from one site to another may take place giving high conduction. One typical example is α -AgI where the number of sites per unit cell is 12 as against the number of ions which is 2. So the 2Ag⁺ ions can jump freely into the 12 sites available in that unit

TABLE I
Structural parameters of some superionic solids

Material	Structure	No of cation sites/unit cell	No of cations/unit cell	Reference
α -AgI	b c c $a = 5.06 \text{ \AA}$	12	2	Wiedersich and Geller ¹⁶
RbAg ₄ I ₆	Cubic $a = 11.24 \text{ \AA}$	56	16	Wiedersich and Geller ¹⁶ (Isomorphous-KAg ₄ I ₆ and NH ₄ Ag ₄ I ₆)
[(CH ₃) ₄ N] ₂ A ₁₃ I ₁₅	Hexagonal $a = 12.77 \text{ \AA}, c = 26.54 \text{ \AA}$	123	39	Geller and Lind ¹⁷
(C ₅ H ₅ NH) Ag ₅ I ₆	Hexagonal $a = 11.97 \text{ \AA}, c = 7.41 \text{ \AA}$	34	10	Geller ¹⁸ Geller and Owens ¹⁹
α -Ag ₃ SI	b c c (disordered)	12	3	Wiedersich and Geller ¹⁶
Ag ₇ I ₄ PO ₄	Cubic $a = 10.6 \text{ \AA}$	—	—	Takahashi <i>et al.</i> ²⁰
(C ₅ H ₅ NH) ₂ Cu ₅ Br ₇	Space group P ₂ , ₂ , ₂ $a = 13.09 \text{ \AA}, b = 11.04 \text{ \AA}$ $c = 11.78 \text{ \AA}$	52	20	Chan and Geller ²¹
Li ₂ SO ₄	f c c $a = 7.07 \text{ \AA}$ at 610 °C	3	2	Forland and Krogh-Moe ²²
Li ₄ SiO ₄	Monoclinic	18	8	Vollenkle <i>et al.</i> ²³

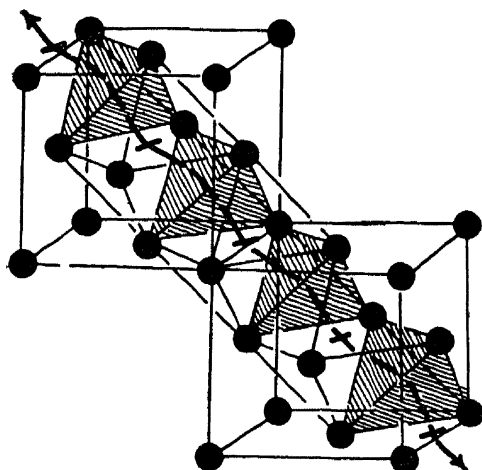


FIG 1 An almost linear passage way in an fcc anion lattice.

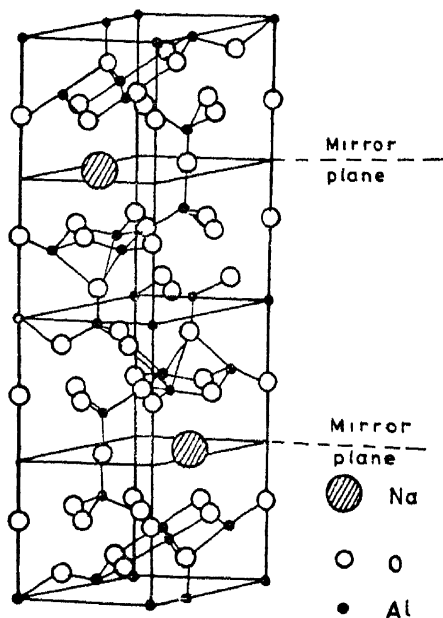


FIG 2 Crystal structure of β -alumina primitive unit cell

cell. For mobility between cells a face shared polyhedra provides the channelled structure given in Fig 1. Another interesting example is that of β -alumina (Fig. 2) where the low percentage occupancy for each site is also present. β -alumina has a layered structure in which there are three categories of cationic sites referred to as B-R, α -Br sites, mid oxygen (m o) sites²⁴ possessing different percentage occupancies.

SPECIAL PROBLEMS OF PROTON TRANSPORT

As discussed above, two important criteria for high ionic conductivity are that the moving ion must be monovalent with small ionic radii. Both these criteria are satisfied for H^+ ion, yet there are not many good proton conductors available. Some of the special problems of proton conduction are listed below²⁵

- (i) Naked H^+ ions are not found in solids under equilibrium condition ($\tau > 10^{-11}$ sec). H^+ is always covalently bonded to some electronegative atoms/ions in the structure e.g. C-H, N-H, O-H.
- (ii) Protons can be shared between two electronegative atoms e.g., O-H-O. This is the so-called hydrogen bond.
- (iii) Oscillation of H from one side to the other in a hydrogen bond $O-H-O \rightleftharpoons O-H-O$ corresponds to a net transport of charge and is, therefore, an essential step in the proton conduction mechanism.
- (iv) Proton conduction differs from the conduction of other ions (Na^+ , K^+ , Ag^+) principally in the following ways.

- (a) Hydrogen bond is covalent and directional in character, whereas metal ions in ionic solids experience coulomb forces more or less from all sides
- (b) As a consequence, proton conduction involves at least two different steps as opposed to one step process for the other metal ion conduction.

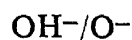
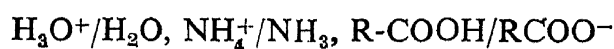
Different suggested transport mechanisms for proton conduction in solids are .—

(i) *Liquid-like Transport*

Liquid-like transport is possible in (a) materials which contain water layers included in the crystal structure such as H-montmorillonite, H-Al-Montmorillonite and H-Al-Fe-montmorillonite clay ²⁶ In these materials (clays) interlayer water forms liquid-like network permitting high protonic conductivity due to the liquid-like motion of H^+ (b) Polycrystalline materials composed of charged crystallites held together by an electrolyte solution.

(ii) *Proton Jump followed by Reorientation*

This mechanism will function with the following acid/base couples properly located at alternating positions



The proton jump is possible by tunnelling in a hydrogen bond The mechanism involves two steps as follows —

- (i) In the first step the proton is transported by tunnelling (or hopping) in hydrogen bond (e g., $H_3O^+ \rightarrow H_2O$, $NH_4^+ \rightarrow NH_3$ etc).
- (ii) In the second step, the subsequent reorientation of neutral molecules (e g H_2O , NH_3 .) thus formed to occupy the vacant proton positions

The molecular reorientation during proton conduction is shown in Fig 3 as an example for hydrogen uranyl phosphate ($HUO_2 PO_4 \cdot 4H_2O$) In this material, which is 'acidic hydrate', alternating layers of UO_2^{2+} and PO_4^{3-} ions contain layers of H_2O

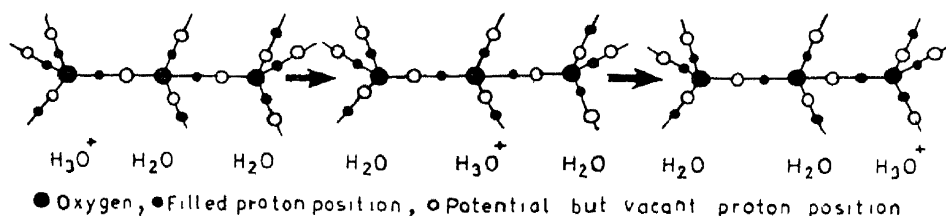


FIG 3 Illustrative example of proton motion in $HUO_2PO_4 \cdot 4H_2O$

and H_3O^+ ion. The ratio of H_3O^+ to H_2O is 1 to 3 where hydrogen bonding is dominating. Other examples of acid hydrate group are $\text{H}_2\text{UO}_2 \cdot \text{AsO}_4 \cdot 4\text{H}_2\text{O}$, $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 29\text{H}_2\text{O}$ and $\text{H}_3\text{PMo}_{12}\text{O}_{40} \cdot 29\text{H}_2\text{O}$,²⁸ $\text{H}_3\text{O} \cdot \text{Al}_3(\text{SO}_4)_2 \cdot (\text{OH})_6$,²⁹ $\text{H}_8\text{UO}_2(\text{IO}_6)_2 \cdot 4\text{H}_2\text{O}$,³⁰ H_3O^+ - β -alumina etc.³¹

Another example is that of a basic hydrate $[\text{Zn}_2\text{Cr}(\text{OH})_6] \cdot \text{OH} \cdot n\text{H}_2\text{O}$ ³² which shows conduction due to proton exchange between H_2O and OH^- species. Here in the positively charged layers of $[\text{Zn}_2\text{Cr}(\text{OH})_6]^+$, the interlayer of $[\text{X} \cdot n\text{H}_2\text{O}]^-$ are present, $[\text{X}^- = \text{OH}^-]$. Similar is the case for other acid/base groups. The transport phenomena is known as 'Grotthius type mechanism'. The activation energy lies entirely in the reorientation step. Thus, net activation energy is low.

(iii) Polyatomic Ion Transport

This type of conduction prevails in compounds, where the corresponding acid/base partners are not present i.e., H_3O^+ without excess H_2O , OH^- without O^{2-} or H_2O , and NH_4^+ without NH_3 are present in the material. The polyatomic ions H_3O^+ , OH^- or NH_4^+ migrate as entities through the bulk material. The activation energy is expected to be very high. This is known as 'vehicle mechanism'.³³ In solids like $\text{LiN}_2\text{H}_5\text{SO}_4$,³⁴ H_3O^+ - β -alumina and NH_4^+ - β -alumina,³⁵ NH_4^+ -Zeolite,³⁶ $\text{H}_3\text{O} \cdot \text{UO}_2 \cdot \text{AsO}_4 \cdot 3\text{H}_2\text{O}$ ³⁷ polyatomic species like H_3O^+ , N_2H_5^+ , NH_4^+ etc. migrate as entities on application of electric field.

The 'vehicle mechanism' and 'Grotthius mechanism' are pictorially illustrated in Fig 4.

MATERIALS

The various protonic conductors can be classified as —^{1,2}

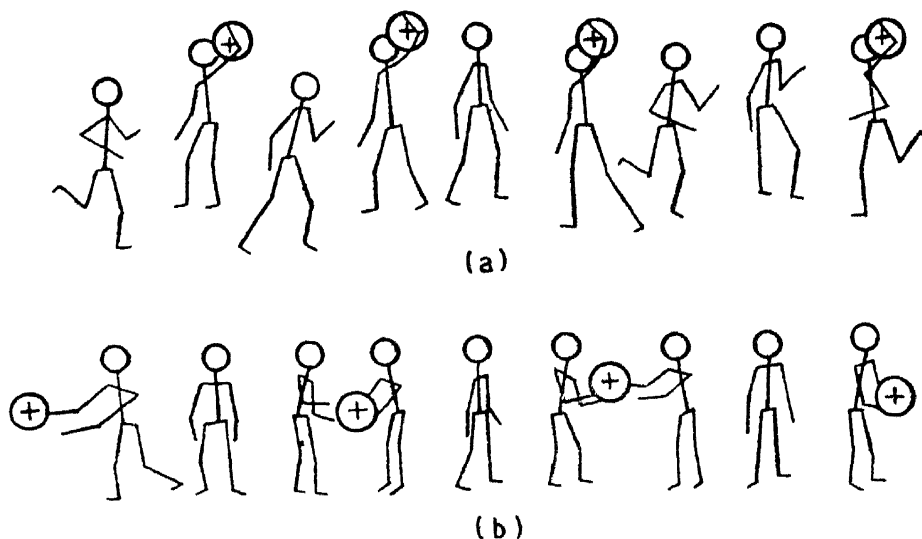


FIG 4 (a) Polyatomic ion transport or "Vehicle mechanism"

(b) Co-operative ion motion (with reorientation + hopping) or Grotthius mechanism

A Non-Hydrogen-Bonded Systems

(i) Materials lacking stoichiometric hydrogen in which proton occurs either by defect equilibria with water and/or hydrogen or secondly by electrical injection of protons from adjacent layers. A few metal oxides like Cu_2O , CoO , NiO , ZnO , TiO_2 etc may sustain protons $\sim 10^{-5} - 10^{-7}$ mole fraction.

(ii) Aromatic hydrocarbons without hydrogen bonds are also possible candidates for proton conduction. However, not many compounds have been reported. Anthracene probably has some protonic conduction.

B. Hydrogen-Bonded Systems

(i) Isolated hydrogen bonds in small carboxylic acids, hydroxy compounds (orthoboric acid H_3BO_3 , pentaerythritol etc), alkali metal fluorides (like KHF_2) allow some proton conduction.

(ii) A large group of materials with chains of hydrogen bonds broken by intramolecular links have been found to show proton conduction like NH_4Cl , $(\text{NH}_4)_2\text{SO}_4$, ammonium perchlorate, oxonium perchlorate, triglycine sulfate (TGS), the KDP ferroelectric family, amino acids, a few hydrates, borax, imidazole etc.

(iii) A few materials with linked chains of hydrogen bonds also show protonic conduction like ice, alcohols etc.

C Organic Polymeric Systems

Polyamides (nylon), polysulphinimide $(\text{SONH})_n$, mylar etc, are some familiar examples.

D Biological Systems, Including Biopolymers

Some of the proton conductors are listed in Table II.

SOME EXPERIMENTAL RESULTS

We wish to discuss some unusual results recently obtained by us on two hydrates viz Molybdic acid, $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ and Ammonium para-tungstate $(\text{NH}_4)_{10} \cdot \text{W}_{12} \cdot \text{O}_{41} \cdot 5\text{H}_2\text{O}$. Glasser² has identified some important experimental techniques necessary for the study of proton conductors. A major problem in the field of proton conductor is a definite proof that charge transfer in the solid occurs by motion of protons. Some of the techniques used are —

- Time-dependent polarisation (including Maxwell-Wagner dispersion)
- Coulometric measurement
- Space-charge Polarisation
- Electrical conductivity and thermoelectric power
- Diffusion
- Ion Dynamics by NMR, IR, Raman, Electron paramagnetic resonance, Neutron scattering etc

TABLE II

Materials	Sp Conductivity (ohm ⁻¹ cm ⁻¹) at room temp	Proton Conduction Mechanism
(i)	(ii)	(iii)
1. H ₂ UO ₂ PO ₄ ·4H ₂ O (HUP)	4 × 10 ⁻³	H ₃ O ⁺ /H ₂ O jump
2. H ₂ UO ₂ ASO ₄ ·4H ₂ O (HUAs)	6 × 10 ⁻³	H ₃ O ⁺ /H ₂ O jump
3. H ₂ UO ₂ (IO ₆) ₂ ·4H ₂ O	7 × 10 ⁻³	H ₃ O ⁺ /H ₂ O jump
4. Sb ₂ O ₅ ·nH ₂ O	3 × 10 ⁻⁴	H ₃ O ⁺ /H ₂ O jump
5. (H ₂ O) Al ₃ (SO ₄) ₂ (OH) ₆	3 × 10 ⁻⁴	H ₃ O ⁺ /H ₂ O
6. Sb ₂ O ₅ ·4H ₂ O	10 ⁻³	H ₃ O ⁺ /H ₂ O jump
7. [H(H ₂ O) _n] ₁₂ Sb ₁₂ O ₃₆	10 ⁻⁷	H ₃ O ⁺ /H ₂ O jump
8. H ₃ OUO ₂ ASO ₄ ·3H ₂ O	—	H ₃ O ⁺ /H ₂ O at high pressure H ₃ O ⁺ migration at low pressure
9. [Zn ₂ Cr(OH) ₆]OH·nH ₂ O	6 × 10 ⁻⁴	H ₂ O/OH ⁻
10. β-KOH (248 °C)	10 ⁻³	H ₂ O/OH ⁻
11. H ₃ PMo ₁₂ O ₄₀ ·29H ₂ O (PMA)	1.8 × 10 ⁻¹	Liquid like transport of H ⁺
12. H ₃ PW ₁₂ O ₄₀ ·29H ₂ O (PWA)	1.7 × 10 ⁻¹	Liquid like transport of H ⁺
13. H ⁺ montmorillonite clay	1.4 × 10 ⁻⁴	Liquid like transport of H ⁺
14. H-Al montmorillonite clay	10 ⁻⁴ –10 ⁻²	Liquid like transport of H ⁺
15. MoO ₃ ·2H ₂ O	10 ⁻⁵	Liquid like electrolysis
16. In(OH) ₃ ·4H ₂ O	10 ⁻³	Liquid like transport of H ⁺
17. (NH ₄) ₁₀ W ₁₂ O ₄₁ ·5H ₂ O	10 ⁻⁶	—
18. Al(OH) ₃ ·4H ₂ O	6 × 10 ⁻⁸	Liquid like transport of H ⁺
19. Ca ₂ O ₃ ·4H ₂ O	10 ⁻⁴	Liquid like transport of H ⁺
20. SnO ₂ ·3H ₂ O	2 × 10 ⁻⁴	Liquid like transport of H ⁺
21. ZrO ₂ ·23H ₂ O	3 × 10 ⁻⁵	Liquid like transport of H ⁺
22. H ₂ O ClO ₄	3 × 10 ⁻⁴	H ₃ O ⁺ migration of impurity conduction
23. Hydrated hydronium β-alumina	5 × 10 ⁻³	H ₃ O ⁺ /H ₂ O jump H ₃ O ⁺ migration
24. NH ₄ ⁺ -β-alumina	10 ⁻³	NH ₄ ⁺ migration
25. NH ₄ ⁺ -zeolite	2 × 10 ⁻³	NH ₄ ⁺ migration
26. LiN ₂ H ₅ SO ₄	2 × 10 ⁻⁸	N ₂ H ₅ migration
27. SnCl ₂ ·2H ₂ O	10 ⁻⁶	Liquid like transport
28. (NH ₄) ₂ H(SO ₄) ₂	10 ⁻³	—
29. LiH ₂ PO ₄	10 ⁻³	R-PO ₃ H/R-PO ₃ ⁻
30. SrCe _{1-x} M _x O ₃ (600 °C) (M = Y, Yb, In, Zn, Nd)	10 ⁻²	Conduction by electron holes
31. N ₂ H ₆ SO ₄ (200 °C)	10 ⁻⁴	Reorientation followed by hop

It must be, however, noted that no single technique would be able to tell unambiguously about the proton transport. A combination of many techniques may reasonably decide the transport mechanism. Some of the more common techniques are:

(a) Coulometric Measurement

When current is passed between electrodes holding the sample, the electrochemical product of the conduction in the form of gas at the negative electrode is

collected and measured. The percentage of charge carried by the protons can be calculated from the volume (and hence the mass) of gas collected.

(b) *Nuclear Magnetic Resonance*

The dynamics of proton motion in solids is best studied by NMR. A 'line-narrowing' occurs when the proton is free to move. Further, the relaxation time measurements also help in knowing the detailed ion dynamics.

(c) *IR and Raman Spectra*

The presence of low frequency modes in laser Raman spectra are generally indicative of a free-ion situation. Sometimes, the IR spectrum is also found to be broadened and modified as a result of proton-tunneling or weakening of hydrogen bond. Chandra and Singh³⁸ tried to locate the mobile H^+ by looking at the IR spectra of original sample and a sample from which some protons have been transported out by electrolysis during coulometric experiment.

(d) *Neutron Scattering*

Diffuse X-ray and neutron scattering are powerful tools for studying ion dynamics. However, inelastic scattering of slow neutrons is more suited for proton conductors because the incoherent scattering cross-section of hydrogen for neutrons is particularly large.

In the following paragraphs we describe some of the results obtained in our laboratory. The materials fall in the following categories —

- (i) *Hydrates* $MoO_3 \cdot 2H_2O$ and $(NH_4)_{10}W_{12}O_{41} \cdot 5H_2O$
- (ii) *Hydrazine Compounds* $N_2H_6SO_4$ and $N_2H_6Cl_2$

Coulometry and Transference Number

One of the most difficult problems in proton conductors is to show that actually proton is the mobile species. We developed a direct method in which a specially designed coulometer was used and hydrogen evolved was collected (Fig 5). While

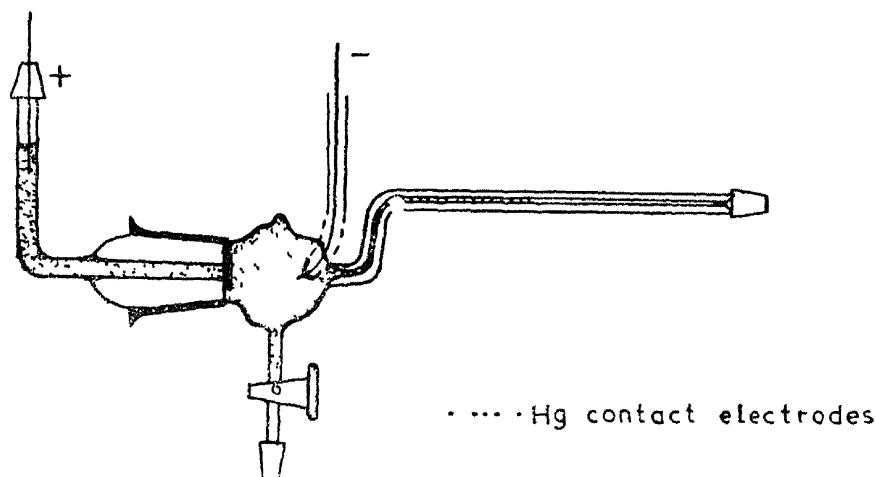


FIG 5 Coulometer

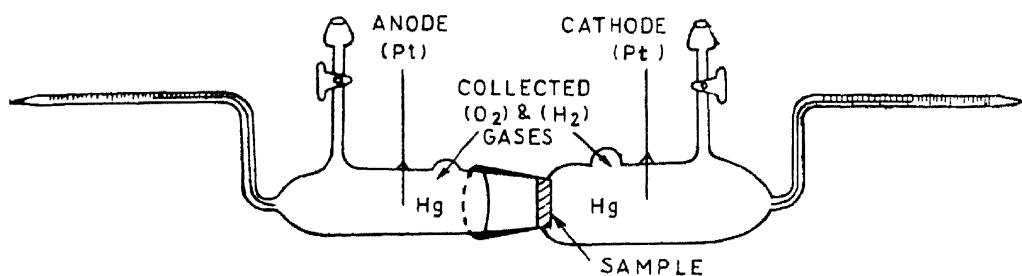


FIG 6 Modified Coulometer or electrolysis cell

carrying out the experiment on $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$, we found that the amount of H_2 evolved at cathode is much less than the expected volume from Faraday's law. We suspected that a part of charge is being carried out by O^{2-} produced as a result of electrolysis. Thus, a new hypothesis of possible electrolysis of interlayer water or water of crystallisation was made. To confirm this, a specially designed coulometer or electrolysis cell was used as shown in Fig 6. The volumes of gases evolved (if any) at cathode/anode could be measured by monitoring the movement of mercury columns in the micro-pipette attached on the two sides. A thin pellet of the sample was mounted by araldite on the cone face separating cathode and anode ends. Electrical contacts at the two faces of the pellets were made with platinum wire electrodes dipped into pure mercury. The electrolysis was carried out at a constant current.

The amount of gases collected (evolved) at the cathode and anode sides of the coulometer are shown in Fig 7 which have been used for calculating the transference numbers. If the material is essentially an ionic conductor with proton as the only mobile species, one would expect H_2 alone to be collected at the cathode as shown in Fig 7. The astonishing result is the evolution of O_2 [Fig 7(a) and 7(b)] and Cl_2 [Fig 7(c)] at the anode. We propose a new concept that the water of crystallisation is electrolysed in the former cases while HCl is electrolysed in the latter case. We have used IR-studies to confirm our electrolysis hypothesis. The effect of electrolysis is most pronounced in $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ where one of the H_2O is interlayer (the other is coordinated) which can be easily electrolysed. For Ammonium paratungstate³⁹ the protons for the transport are mostly provided by NH_4^+ group while only a small part comes from the electrolysis of H_2O . Similarly, in hydrazine di-hydrochloride, the hydrazonium ion provides most of the protons (as established by Chandra and Singh^{38,40} for hydrazine sulphate) and a very small, though finite, part is as a result of electrolysis. The transference numbers for different mobile ionic species in the above studied four compounds are: Molybdic acid ($t_{\text{H}} = 0.69$, $t_{\text{O}_2} = 0.18$), ammonium paratungstate ($t_{\text{H}} = 0.79$, $t_{\text{O}_2} = 0.14$), hydrazine di-hydrochloride ($t_{\text{H}} = 0.92$, $t_{\text{Cl}} = 0.07$), hydrazine sulfate ($t_{\text{H}} = 0.92$).

The transference numbers given above have only limited importance and may actually be in error. When we looked at the sample after the electrolysis experiment was completed, a blackening of the electrode surfaces was noted. This is indicative of some electrode reaction. The possible reactions for $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ are as follows

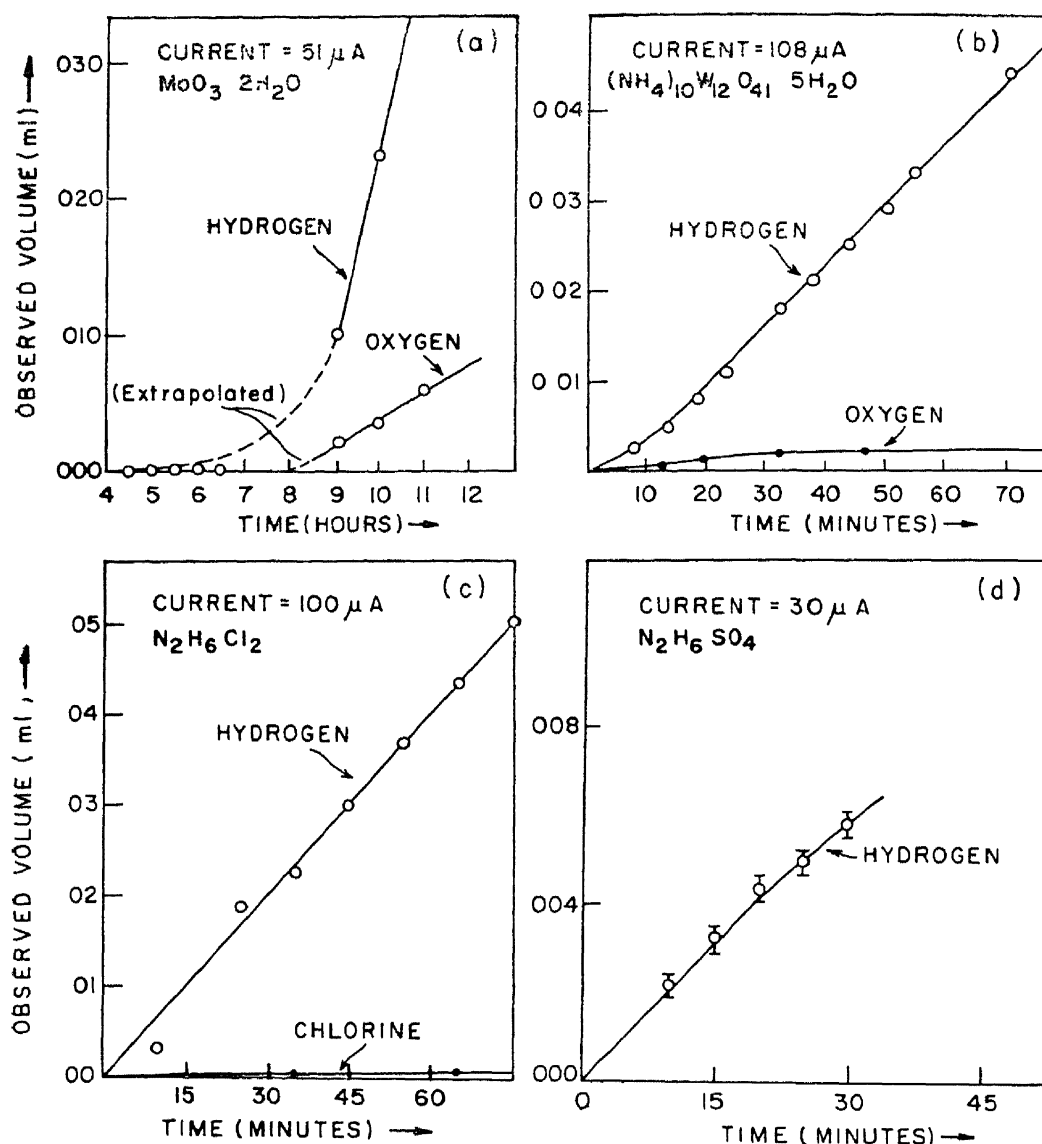


FIG 7 Volume of gases evolved as a function of time

At cathode $x\text{H} + \text{MoO}_3 (\text{group}) \rightarrow \text{H}_x\text{MoO}_3$ Bronze (Blue/Grey)

At anode $\text{Hg} + 1/2\text{O}_2 \rightarrow \text{HgO}$

We could not definitely identify the presence of HgO for MoO₃ · 2H₂O case from IR spectroscopy as the new peak position $\sim 1000\text{ cm}^{-1}$ coincided with one of the bands of the monohydrate MoO₃ · H₂O (resultant electrolysis product). However, this band could be seen in material near the anode surface after the electrolysis of (NH₄)₁₀W₁₂O₄₁ · 5H₂O³⁹

Infrared Studies of Electrolysed Sample^{39a,b}

In an attempt to identify the hydrogen which has moved out of the sample during electrolysis, we have taken the infrared spectra of electrolysed sample and compared it with the IR spectra of the original sample. These spectra are given in Fig 8. Laser Raman spectra of some of the samples have also been taken and would

be reported elsewhere. The salient features relevant to the present discussion are given below.

The IR spectra of original $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ and the material obtained after electrolysis or coulometry experiment are shown in Fig 8(a). A comparison of band

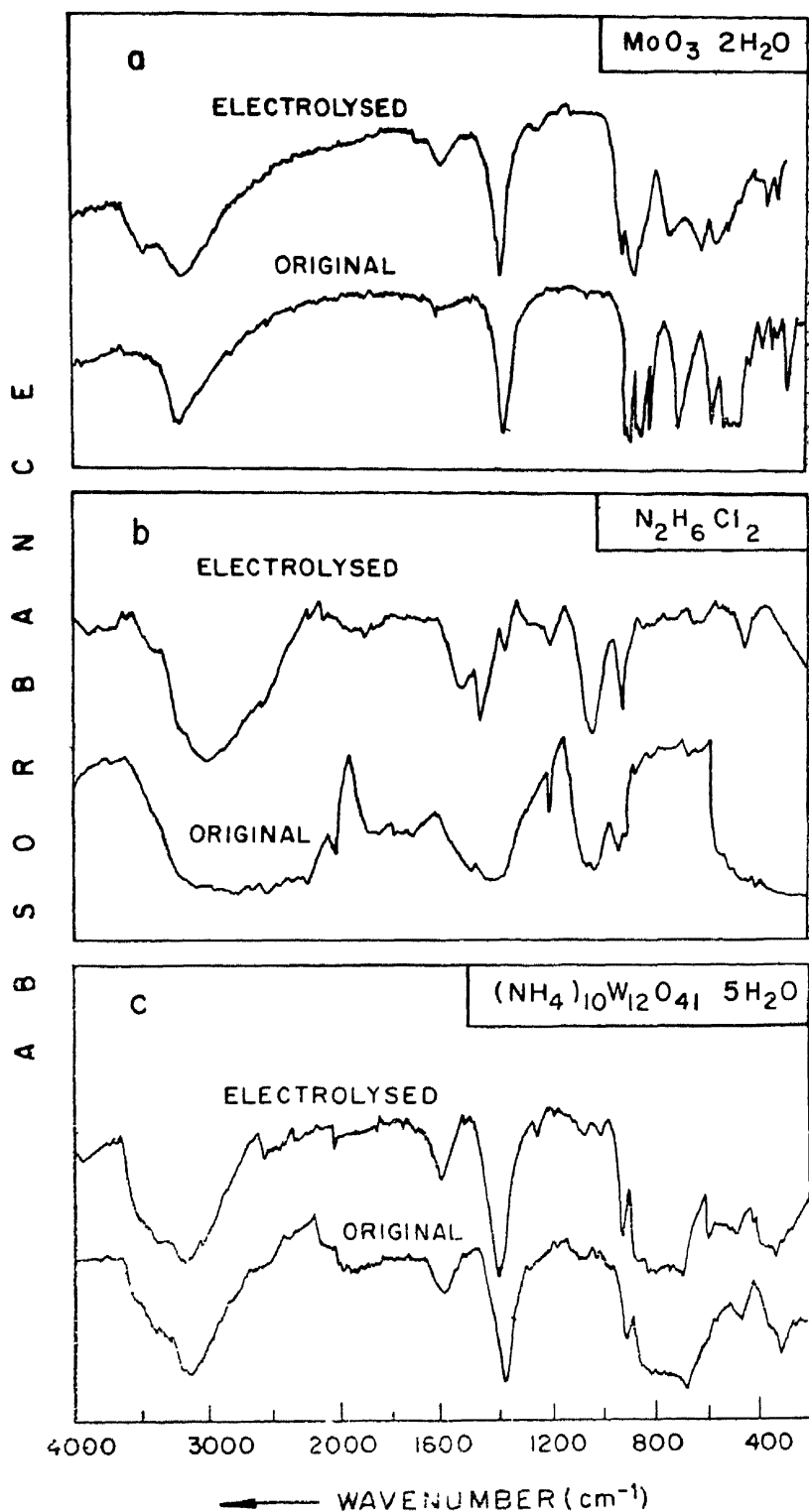


FIG 8 IR absorption spectra of the original and electrolysed samples

positions of these recorded spectra with those already reported in the literature⁴¹⁻⁴³ shows that the electrolysed material consists of $\text{MoO}_3 \cdot \text{H}_2\text{O}$ (monohydrate). This confirms our hypothesis of electrolysis of molybdic acid in which the dihydrate has been converted into monohydrate.

Fig 8(c) gives similar results for ammonium paratungstate. The most distinctive feature is the appearance of two new peaks around 1240 and 3000cm^{-1} in the electrolysed sample. This may be due to lifting of degeneracy as a result of the lowering of symmetry of any particular molecule or ion after electrolysis. We have hypothesized in our coulometry studies on this material that NH_4^+ group provides most of the protons for transport while only a part of it is provided by electrolysis of hydrated water. NH_4^+ ion has T_{2h} symmetry while NH_3 has C_{3v} symmetry. This lowering of symmetry results in one additional bending peak of NH_3 at 1240 cm^{-1} and N-H stretching peak at 3000 cm^{-1} .

Fig 8 (b) gives IR spectra of $\text{N}_2\text{H}_6\text{Cl}_2$ or $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$. In coulometry we have collected a very small amount of Cl_2 and so most of the hydrogen evolved is not essentially due to electrolysis of HCl group. The IR spectra shows appearance of new peaks at 1400 cm^{-1} and 1235 cm^{-1} and some other features which are characteristics of N_2H_5^+ group confirming the removal of a part of hydrogen from $\text{N}_2\text{H}_6^{++}$ group. Similar results were obtained earlier by Chandra and Singh³⁸ for hydrazine sulphate.

Laser Raman Spectra under D C Bias

Laser Raman spectra (Fig 9) of the original sample ($\text{MoO}_3 \cdot 2\text{H}_2\text{O}$) without electrolysis and during electrolysis near cathode and anode separately were recorded at different intervals of time with d.c. bias 'on'. The main differences between the Raman spectra of the original and the electrolysed samples near cathode and anode are given below —

(i) Two new modes appear at 795cm^{-1} and 414cm^{-1} . These bands grow with time of electrolysis as given in Fig 10. Further, the recorded spectra at the cathode during electrolysis resembles with the reported laser Raman spectra of white or α - $\text{MoO}_3 \cdot \text{H}_2\text{O}$ by Saleem and Aruldas⁴³ which confirm our earlier IR studies.

(ii) The relative intensities of pair of bands, viz 77cm^{-1} and 88cm^{-1} which are related to translational motion of ions, change. This is more evident in samples near cathode.

(iii) The relative intensities of 888cm^{-1} band and water libration mode 846 cm^{-1} also change.

NMR under D C Bias

Here, we describe an unusual method for studying ion transport. It is well known that NMR line narrowing occurs in the presence of rotational and/or translational diffusion. Our effort here was to look for the motion of H^+ under d.c. field. To

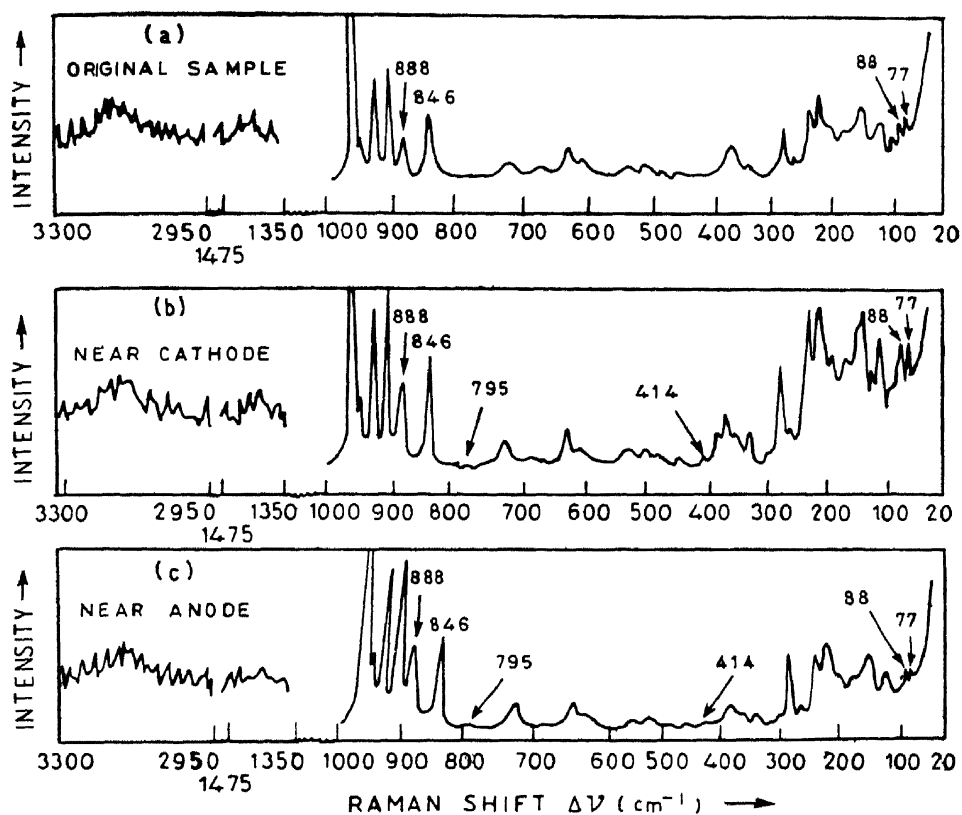


FIG 9 Laser Raman spectra of (a) original sample ($\text{MoO}_3 \cdot 2\text{H}_2\text{O}$) without field, (b) sample at cathode when d.c. electrolysis is in progress at 20 volts and (c) sample at anode when d.c. electrolysis is in progress at 20 volts

detect a possible translational diffusion of H^+ we measured NMR line width as a function of applied d.c. bias across the sample. This has been presented earlier by us.⁴⁴ NMR line width measurements were made on pressed cylindrical samples of $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ placed inside a glass tube. These aquadag silver electrodes were placed on two opposite faces of the pellets. Copper/Silver wire leads were attached to this. ^1H NMR spectra of these samples were recorded at different d.c. bias with the help of a wide line NMR spectrometer at 9.6 MHz. We quote here some of the results reported earlier by us.⁴⁵

The peak to peak linewidths of the recorded derivative signals corresponding to Proton magnetic resonance absorption lines of $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ pressed pellets under increasing d.c. bias at different temperatures were measured separately. Following significant observations were noted:

(i) At $(125 \pm 25)^\circ\text{K}$ the observed derivative signals were found to be highly uniform and symmetric [Fig. 11 (a)]. The measured linewidth was approx. equal to 3.0 Gauss, being independent of increasing d.c. bias at this temperature. This leads us to conclude that at this temperature both water protons behave in similar way.

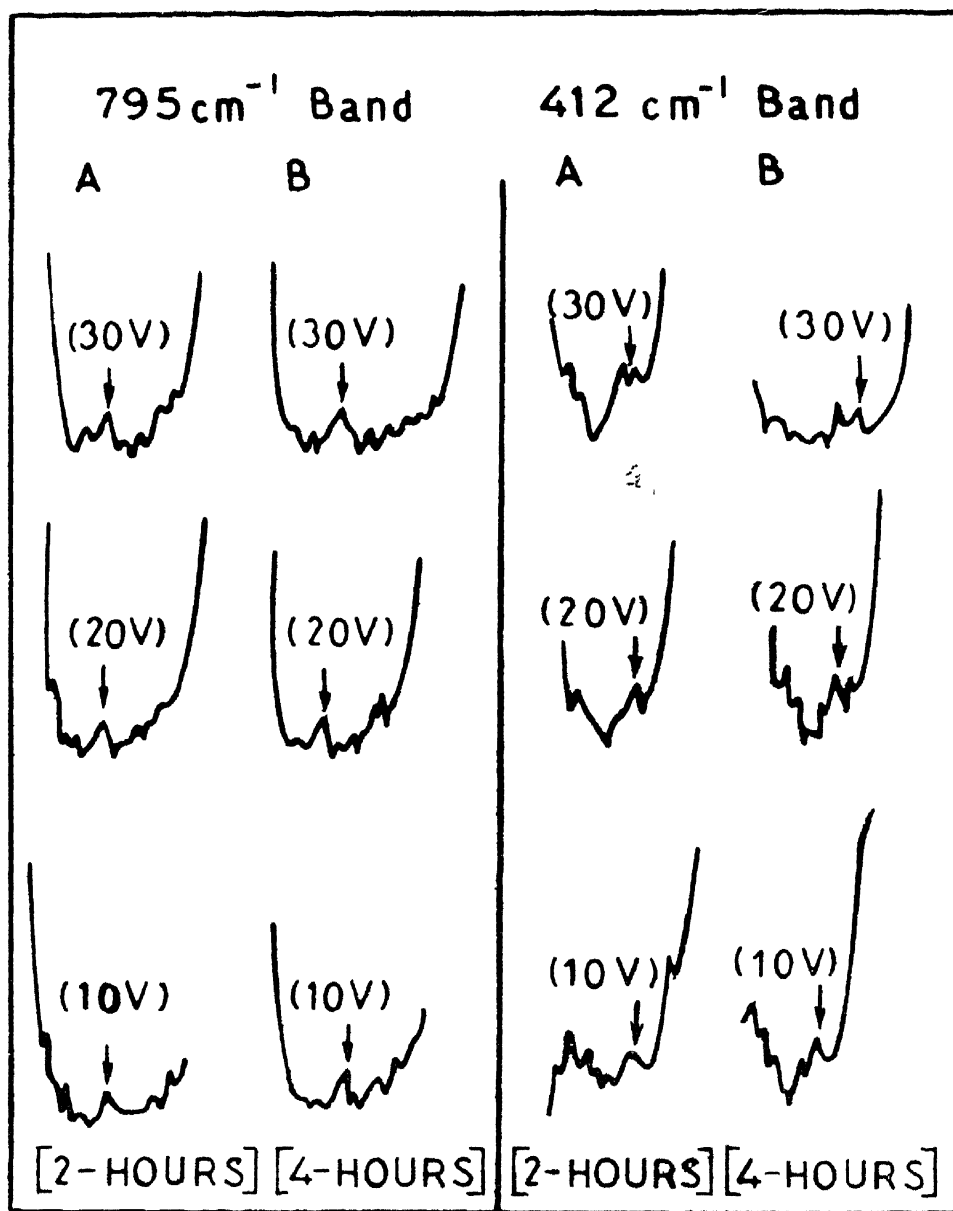


FIG 10 Growth of 795cm^{-1} and 412cm^{-1} bands with electrolysis time near cathode

(ii) With increasing temp (from 300 to 373 °K), unique asymmetric derivative signals appear. The symmetry is found to be broken at points P_1 and P_2 marked by arrows on the derivative curves as shown in Fig 11(b) for $V = 0$ at 333 °K. This unique shape of the recorded derivative is explained by assuming the superposition of a narrow line shoulder, corresponding to interlayer water protons which are thermally activated in the lattice, over a broad proton resonance line corresponding to the coordinated water molecules being not effected by such temperatures. It is noted that the measured linewidth of the narrow line shoulder (ΔH_2) decreases with increasing temp while that of broad proton resonance line (ΔH_1) remains constant 3.0 gauss. Hence, motional narrowing is associated with shoulder. This suggests that

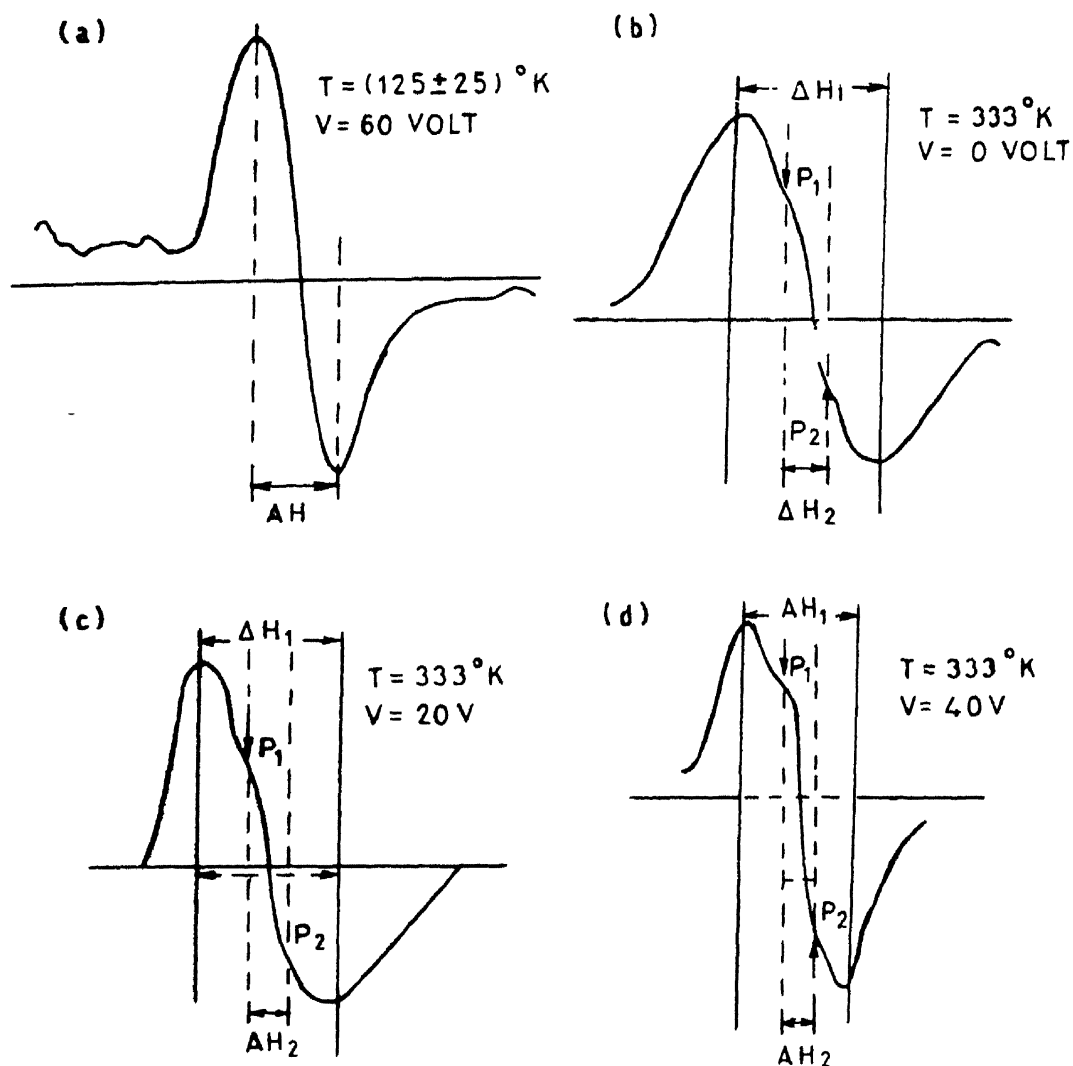


FIG 11 Recorded derivative signals corresponding to proton magnetic resonance absorption lines under different conditions

as a thermally activated process only interlayer water protons take part in the charge transport or conductivity

(iii) With increasing d c bias (0, 20, 40 and 60 volts) at temperatures $(125 \pm 25)^\circ \text{K}$, 300°K and 333°K proton magnetic resonance derivatives have been recorded. One such typical record is shown in Fig 11(c and d) at 333°K . Interestingly, the intensity of the narrow line shoulder seems to increase. The measured linewidths of the narrow line shoulder decrease with increasing d c bias as shown in Fig 12. This suggests that interlayer water protons are made mobile by the applied d c bias. This observation suggests that studying NMR under d c bias can be a useful technique or experimental probe for screening possible proton conductors.

Electrical Conductivity

The detailed investigations of electrical conductivity as a function of temperature and frequency are described elsewhere. Here we describe only those results on

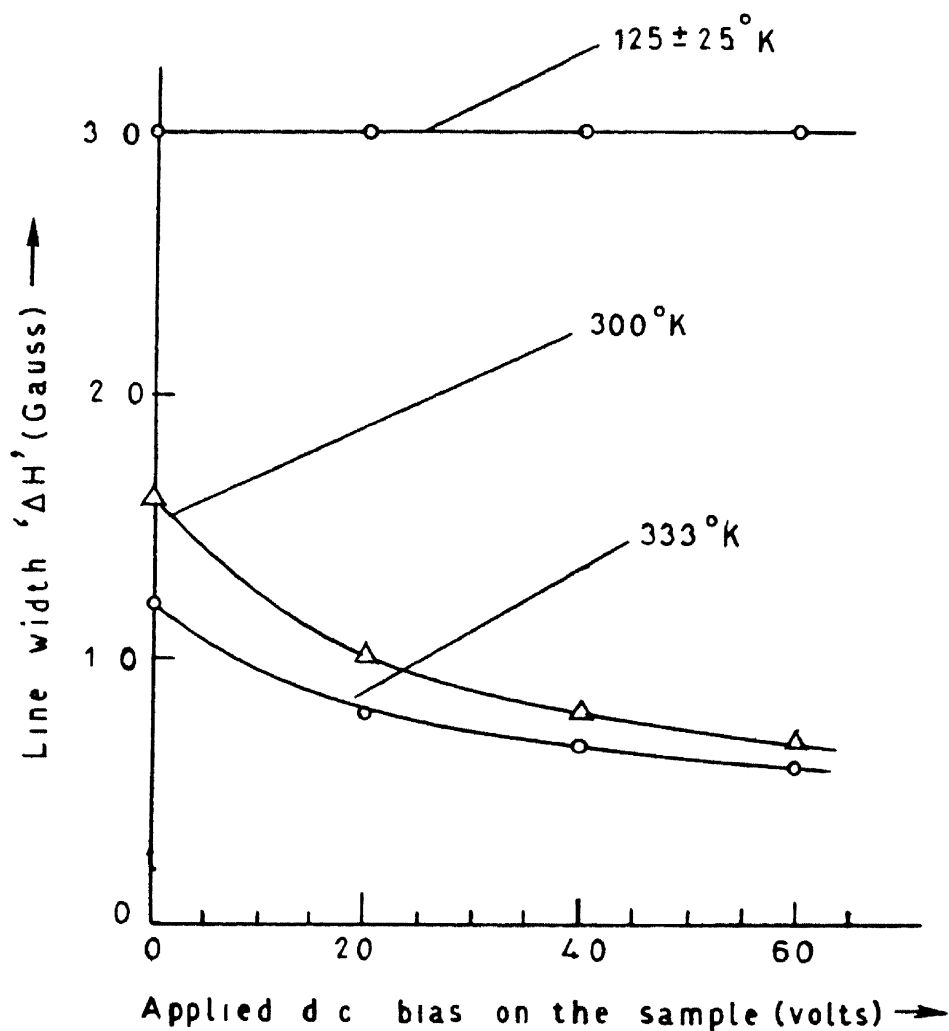


FIG 12

$\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ which are relevant to illustrate our point of view that possible electrolysis of water of crystallization has a role to play in electrical conductivity. If electrolysis is taking place, the number of charged ionic species would increase with d c bias and hence conductivity must increase accordingly. This is found to be true from the experimental results given in Table III.

TABLE III

A C conductivity of $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ at different D C bias⁴⁵

D C Bias in volts	100Hz (ohm ⁻¹ cm ⁻¹)	100kHz (ohm ⁻¹ cm ⁻¹)
0	2.3×10^{-6}	1.5×10^{-5}
0.5	4.7×10^{-6}	2.2×10^{-5}
1.0	6.9×10^{-6}	2.2×10^{-5}
2.0	3.6×10^{-5}	4.1×10^{-5}

Time dependence of a c conductivity has also been investigated. A typical result is shown in Fig 13. The sample was first kept in vacuum. It is found that the conductivity decreases with time partly because of (i) polarisation and (ii) depletion of interlayer water of crystallization as a result of electrolysis. After this, we opened the sample to ambient atmosphere when its humidity is expected to supply the lost interlayer water molecules. As a result, we would expect the recovery of the conductivity as shown by region BC in Fig 13. As a further consequence, the humidity of

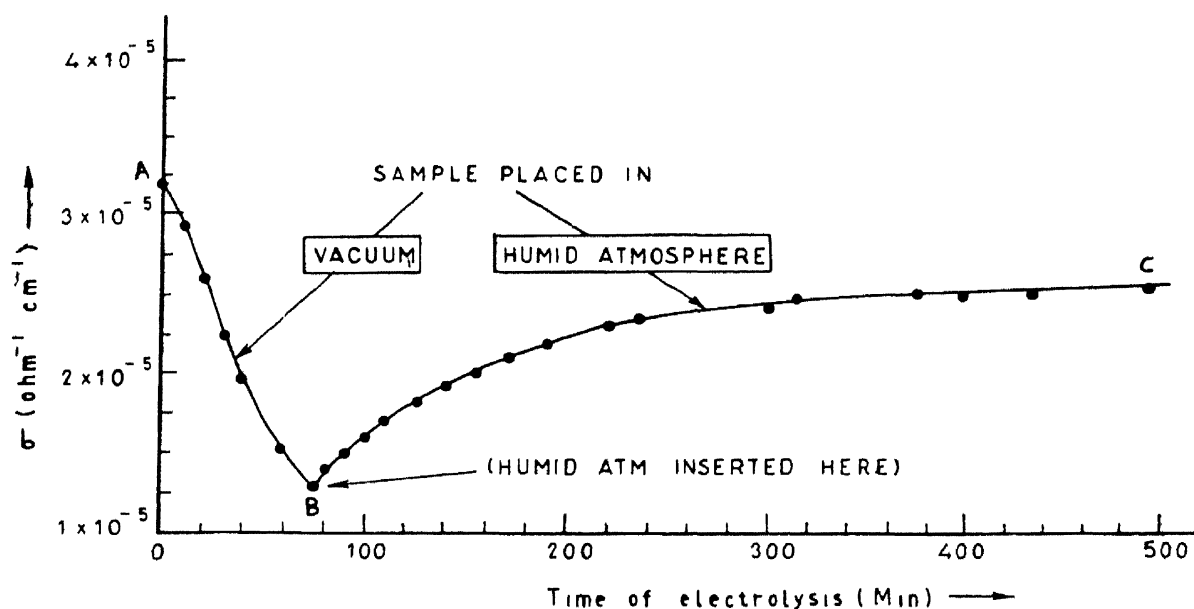


FIG 13 Time dependence of a c conductivity when the sample was kept in vacuum and subsequently in ambient humid atmosphere

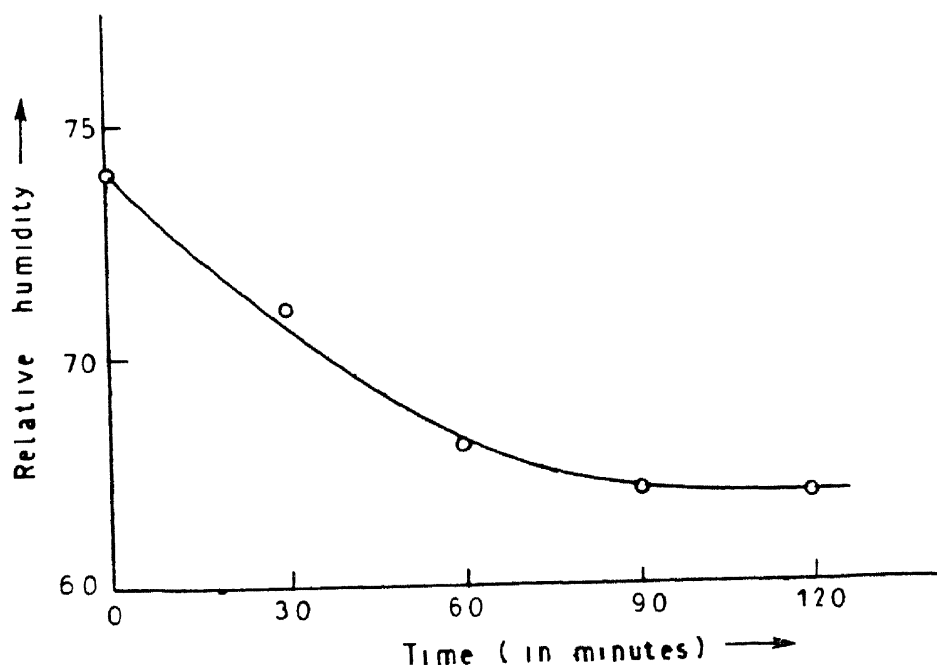


FIG 14 Variation in relative humidity with time

the ambient would decrease. This has led us⁴⁶ to develop a device called solid state dehumidifier.

APPLICATIONS

(1) Solid State De-Humidifier

This works on the principle described earlier according to which a part of interlayer water of crystallisation of solid hydrates can be electrolysed and this loss of water of crystallisation is compensated by diffusion of water molecules from the atmosphere which subsequently leads to dehumidification. The device should be designed such that the end electrodes are able to discharge the electrolysed gaseous products H_2 and O_2 as well as the diffusion of water vapour from outside must be permitted. Pressed pellets of $MoO_3 \cdot 2H_2O$ nearly 2mm thick were used to which a metallic grid (or porous platinum electrode) was attached to act as porous electrode.

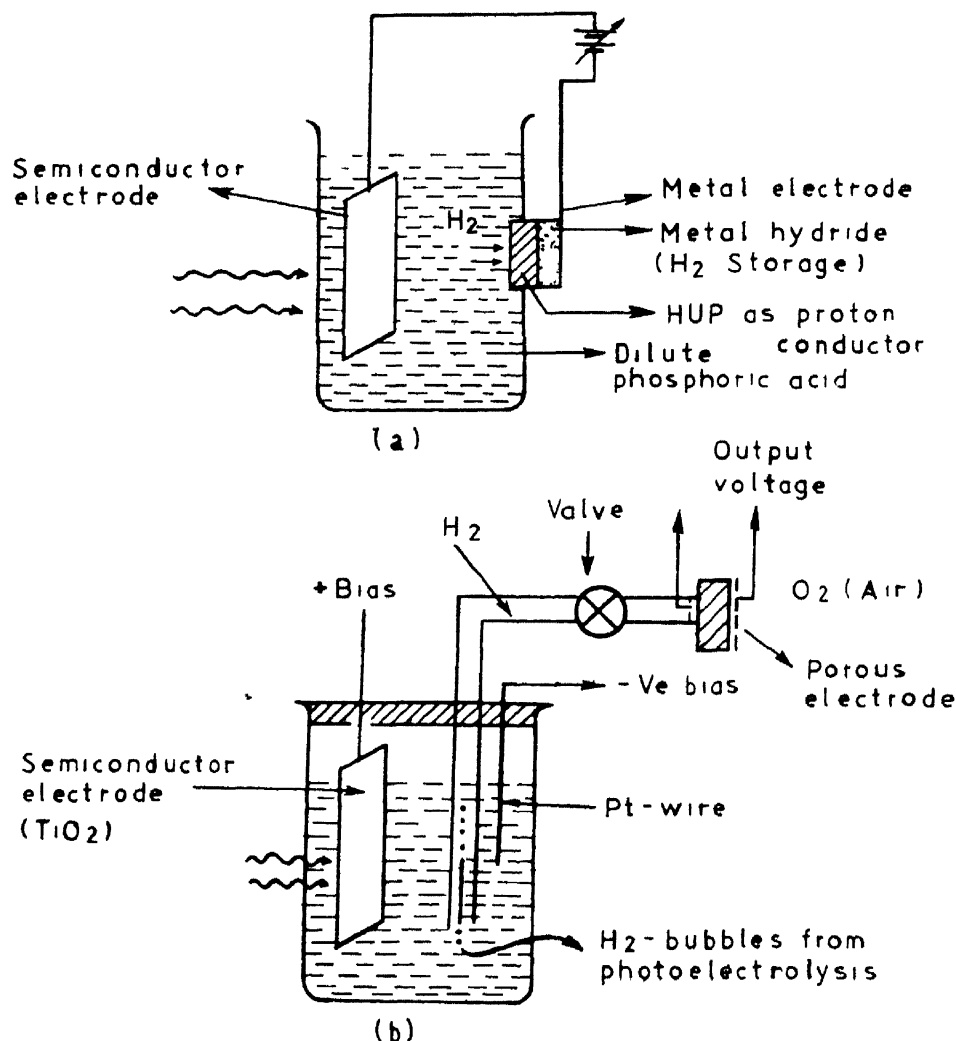


FIG 15 (a) Metal hydride storage of hydrogen produced by photoelectrolysis in PEC
(b) Photoelectrolysis cell integrated with proton fuel cell for *in-situ* storage of solar energy

On application of a small voltage, we found that humidity of the closed enclosure decreased. A typical result is shown in Fig 14

(ii) *Electrochemical Devices*

- (a) Fuel cell
- (b) Proton battery

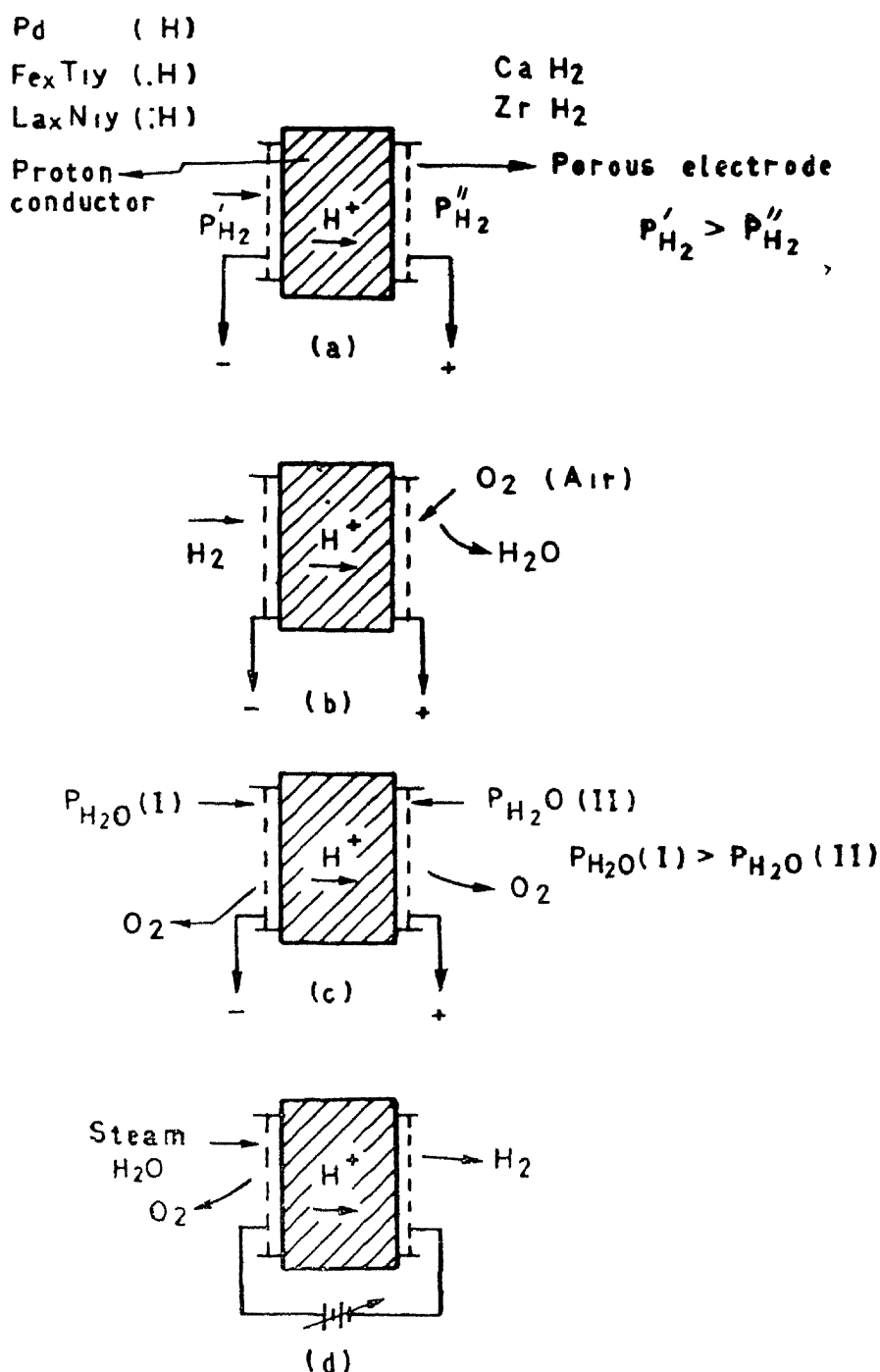


FIG 16 (a) Solid state proton battery (b) H_2 -air fuel cell (c) humidity sensor (d) steam electrolysis cell

(c) Gas and humidity sensors

(d) Steam electrolysis

The principle of the electrochemical device is simple. If the electrochemical activity of the mobile species on the two sides (a_I, a_{II}) of the proton conductors are different, a voltage is developed given by

$$E = \frac{RT}{ZF} \ln \frac{a_I}{a_{II}},$$

where F is Faraday's number and Z is the effective charge on the mobile ion. The activity difference can be created by using different gases on the two sides (H_2/O_2 in fuel cell) or the same gas at different pressures (solid state battery).

Fig. 15 shows schematically these devices. The measurement of electrochemical E M F can also be used to measure the gas pressure (H_2 , H_2O , etc.) on one side of the proton conductor provided the gas pressure or activity at the other end is known. Schematically gas sensors (used as humidity sensors) based on this principle are shown in Fig. 15(c). A novel use of proton conduction is in steam electrolysis. Suppose the proton conductor is biased as in Fig. 15(d). The following cell reaction results in the electrolysis —

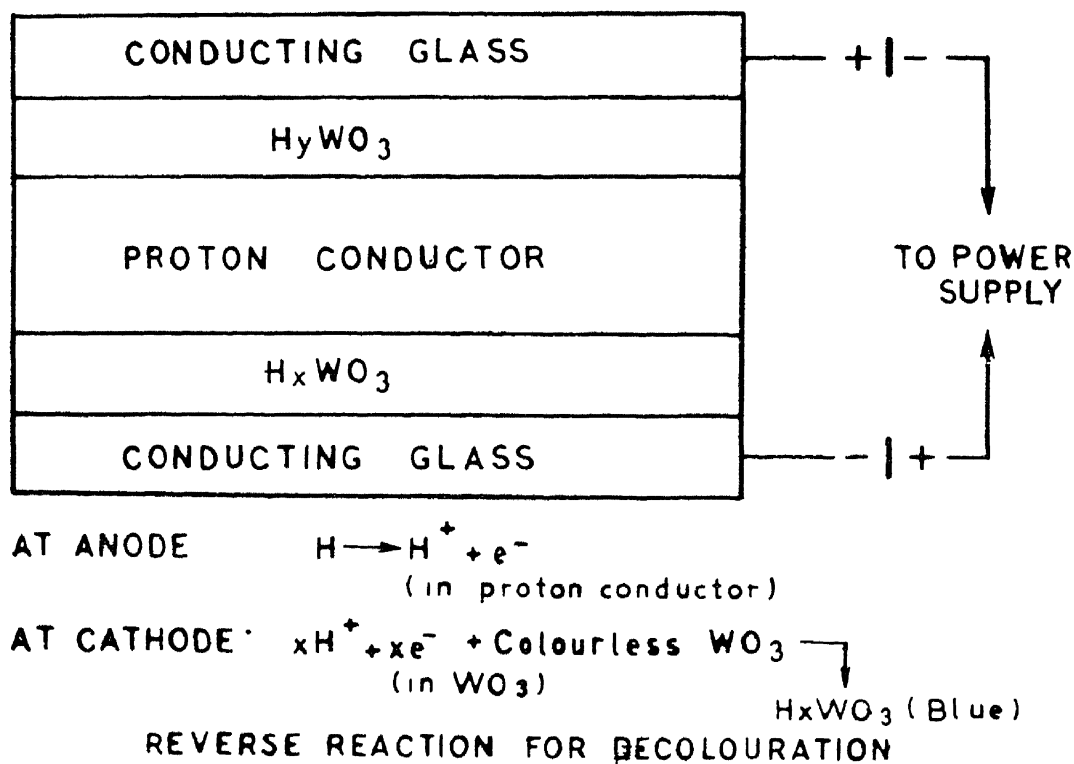
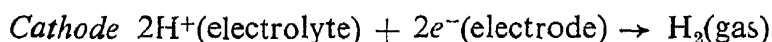
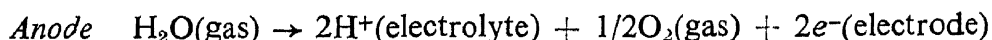


FIG. 17 Schematic diagram of an electro-chromic display device

The pure hydrogen without water vapour can be taken from the cathode compartment

(iii) *Solar Energy Storage*

Recently, Schoonman,⁴⁷ Chandra and Khare (*to be published*)⁴⁸ have integrated the proton conductors into semiconductor-liquid junction photoelectrolysis cell for solar energy storage. The charge transfer between photogenerated electron-hole pairs and the aqueous electrolyte at the semiconductor electrolyte interface results in photoelectrolysis of water and the hydrogen is produced at the metal counter-electrode. In Fig. 16(a) the hydrogen is transported through proton conductor (HUP) and stored in a metal hydride. In Fig. 16(b), the hydrogen produced is collected on one side of the proton conductor to be used in the H_2 /air fuel cell.

(iv) *Electrochromic Display Device*

Fig. 17 illustrates the use of proton conductor in an electrochromic display device. A thin film of colourless WO_3 is coated on the proton conductor.

The device is biased in such a way that hydrogen is transported through the proton conductor which in turn forms a blue brozine H_xWO_3 to give the display. If the bias is reversed, the hydrogen is withdrawn from H_xWO_3 again to give a decoloured WO_3 .

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TRENDS AND PROSPECTS IN ORGANIC SOLID STATE CHEMISTRY

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Recent progress in the area of diffusionless reactions in organic crystals is reviewed, with particular emphasis upon single-crystal to single-crystal transformations; morphology control and absolute configuration determination, and the reactivity of guest molecules incorporated in clathrates and zeolites

Key Words : Organic Solid State Chemistry, Diffusionless Reactions: Single-Crystal-Single-Crystal Transformation; Morphology Control; Absolute Configuration; Guest Molecules in Clathrates and Zeolites

INTRODUCTION

INTEREST in the various transformations (both chemical and physical) which may occur within an organic solid continues to increase. In part, this interest arises from the potential of utilizing the restrictive environment and limited motion available to the reacting molecules towards the synthesis of new and novel materials. At the same time the exploitation of these constrained systems for studying in detail the mechanism of certain reactions has also been pursued. Indeed the range of topics which have been studied is impressive and covers amongst other things, an analysis of the influence of structure on the perfection with which a reaction proceeds,^{1,2} the control of crystal morphology by addition of tailor-made impurities,³ an area of key industrial importance, the determination of absolute configuration,⁴ monitoring the course and identifying the small changes in molecular packing associated with the onset of photoinduced decomposition and abstraction reactions,^{5,6} the influence of the surrounding matrix on the reaction of guest molecules in both clathrates and inclusion compounds² and in inorganic matrices such as zeolites.⁷

Associated with these wide ranging interests a concomitant development of techniques aimed at probing slight changes in structure have also emerged, *in situ* X-ray diffractometry¹—whereby the exact orientation of product molecules within reactant may be determined, Fourier transform infrared—so sensitive that isotopes of very low natural abundance may be studied,⁸ electron spin resonance—giving

the relative orientation and separation of free radical pairs,⁹ and most recently, and with considerable future potential, solid state nuclear magnetic resonance¹⁰ emerging primarily as a result of the realisation that the inherent difficulties associated with the application of NMR to solids may be removed by so-called magic-angle-spinning techniques and with the low natural abundance of ¹³C overcome by cross-polarization procedures

This article will briefly review some of the key areas which are currently being studied in the area of organic solid state chemistry. We shall, in particular, refer to

- (1) Single-crystal → single-crystal transformations, which have been extensively studied in our own laboratory and elsewhere
- (2) Recent trends in the area of so-called "crystal engineering."
- (3) The control of crystal morphology by the addition of small amounts of selected (tailor-made) additives, and the possibility of determining absolute configuration by selective uptake of impurities by particular crystal surfaces
- (4) Recent developments in the area of polydiacetylene chemistry, in particular a method of enhancing the conductivity of such polymers by incorporating dopant molecules into the monomer structure prior to polymerization. The manner in which one may locate these impurity molecules within the lattice is also considered
- (5) The nature of the reactions which occur when organic molecules are converted to product—either thermally or photochemically—within rigid host matrices such as clathrates and zeolites

1 SINGLE-CRYSTAL-SINGLE-CRYSTAL TRANSFORMATIONS AND TOPOCHEMICAL REQUIREMENTS IN [2 + 2] DIMERIZATIONS

Few examples of perfect single-crystal-single-crystal photoinduced reactions are known. In the course of a solid state reaction there is generally a significant change in bond distance and geometry¹¹⁻¹⁵. In the case of the [2 + 2] photodimerization reactions, for example, there is generally either considerable fracture of the crystal during reaction, or else a loss in crystallinity. In both cases the marked change in local geometry results in a loss of lattice control. One particular system, however, which yields highly perfect single-crystal product is based upon¹⁴ 2-benzyl-5-benzylidenecyclopentanone (BBCP), see Fig 1, and several of its derivatives—see Table I.

The crystallographic features associated with this reaction and the associated changes in cell parameters which occur during the transformation have been carefully monitored¹. A gradual change in cell parameter is observed, suggesting that the reaction proceeds smoothly throughout the entire crystal lattice, an observation which may be readily understood by comparing the monomer structure with that

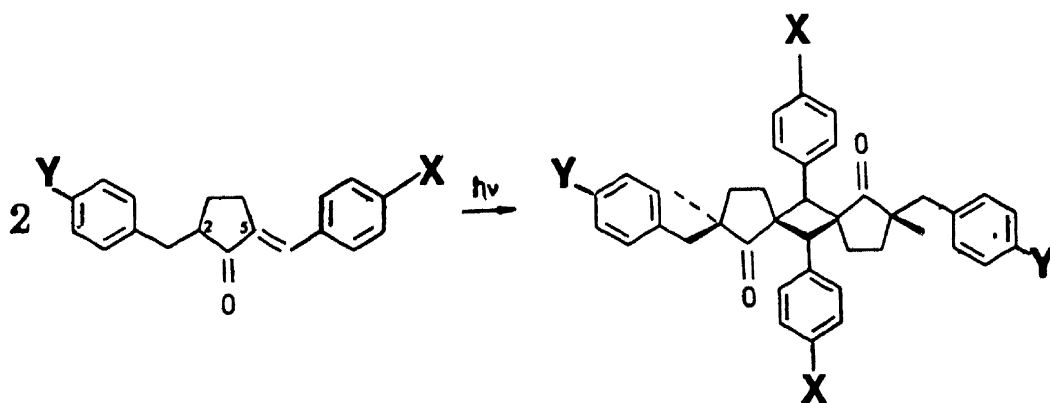


FIG 1 Schematic illustration of the dimerization of BBCP and its derivatives to yield the centrosymmetric product. The changes in cell parameter and space group for various *X* and *Y* substituents are given in Table I

TABLE I

Unit cell values for monomer and dimer crystals for various derivatives of 2-benzyl-5-benzylidenecyclopentanone

X	Y			Space Group	<i>a</i> /Å	<i>b</i> /Å;β(°)	<i>c</i> /Å	<i>V</i> /Å ³
H	H	BBCP	monomer	Pbca	31.302(11)	10.784(3)	8.687(3)	2932
			dimer	Pbca	31.321(4)	10.811(4)	8.629(3)	2922
Br	H	BpBrBCP	monomer	Pbca	34.222(6)	10.923(1)	8.427(1)	3150
H	Cl	pClBBCP	monomer	P2 ₁ /c	17.175(4)	10.587(3)	8.796(5)	1554
						76.33(9)		
H	Me	pMeBBCP	monomer	P2 ₁ /c	17.341(2)	10.675(1)	8.736(1)	1579
						102.54(1)		
Br	Cl	pClBpBr-BCP	monomer	P2 ₁ /c	17.522(4)	7.906(2)	11.888(2)	1646
						91.19(1)		
Br	Me	pMeBpBr-BCP	monomer	P2 ₁ /c	18.381(2)	11.209(2)	8.285(2)	1702
						94.46(1)		
		A	monomer	P2 ₁ /c	17.314(2)	10.667(1)	8.747(2)	1577
						77.39(2)		
			dimeric	P2 ₁ /c	17.306(3)	10.667(2)	8.768(2)	1575
						76.64(2)		

see Fig 1 for position of substituents *X* and *Y* within the molecule

of the product dimer—the space group and crystal packing of the product dimer is identical to that of one of the dimer polymorphs obtained by recrystallization. Fig 2 illustrates the crystal structure of the BBCP monomer viewed along [001], a comparable view of the dimer structure is shown below it. There is clearly little movement associated with the reaction. Indeed, because of the perfection with which the reaction proceeds it transpires that it is possible to obtain full structural

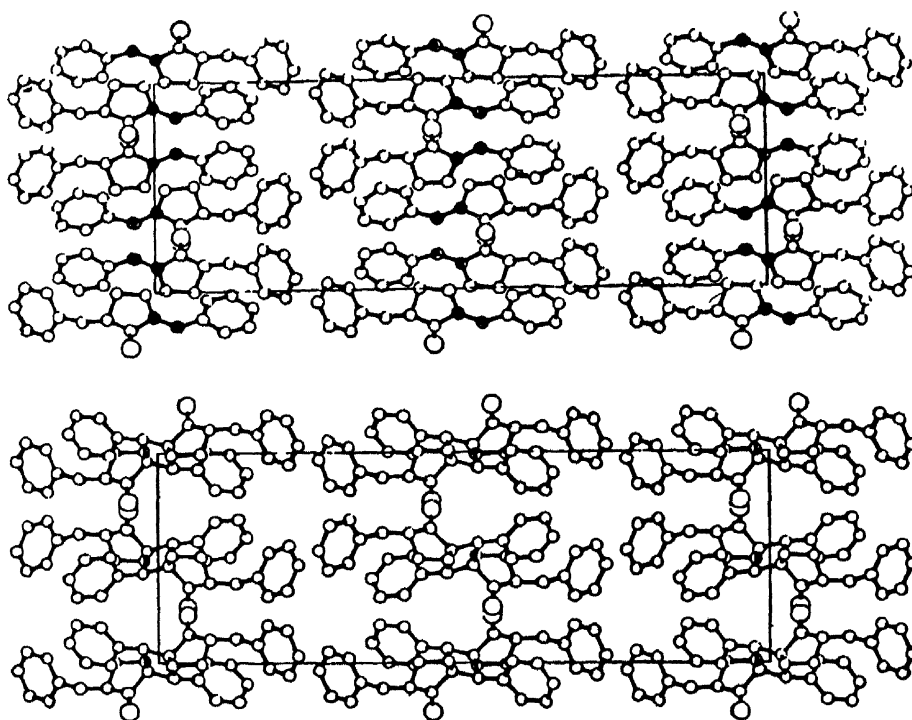


FIG 2 Packing diagram of the monomer of BBCP viewed along [001], upper, and the corresponding view of the dimer product—again along [001] after reaction, lower. carbon atoms C5 and C13 in individual incipient dimer pairs are highlighted

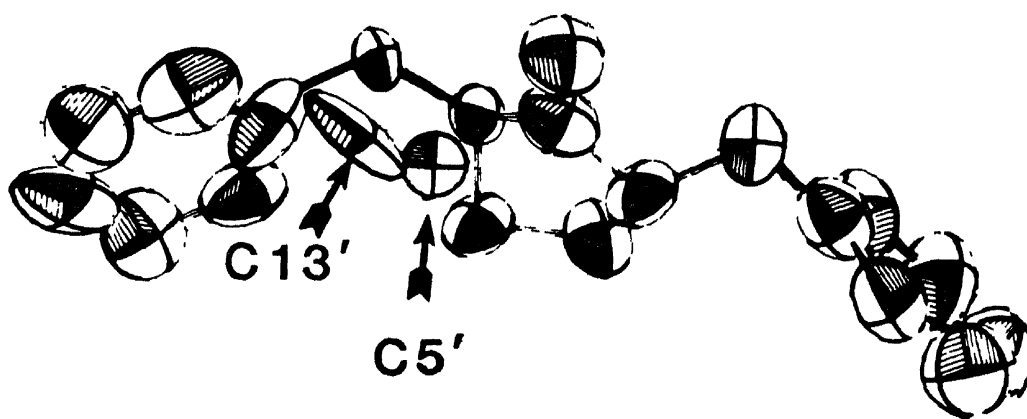


FIG 3 ORTEP plot illustrating the monomer and half-dimer equivalent fragments at approximately 70 per cent conversion—conversions estimated from the refined occupancies of the respective atoms. The thermal ellipsoids are drawn at a 50 per cent probability level, the ellipsoids marked C13' and C5' correspond to the residual monomer within the crystal

data at various stages of the conversion. Fig. 3 shows the situation when 70 per cent of the material has reacted. The structural refinement reveals two locations for the C5 and C13 carbon atoms. One is associated with that component of the crystal which is unreacted, whilst the other corresponds to the dimeric product. Various derivatives, and indeed mixed crystals, have been shown to follow this rather

ideal reaction pathway In most cases the product yield of dimer is, as expected, very close to 100 per cent

For BBCP the photoreactivity may be correlated with the presence, in the monomer structure, of incipient dimer pairs in which the two benzyldiene $C = C$ bonds are related by a center of symmetry, Fig. 4 Intuitively, one might expect this particular arrangement to be a prerequisite for photoreactivity, and loss of such reactivity to arise when the packing mode does not allow either a close-enough approach of the double bonds, or perhaps presents a rather unhelpful relative orientational relationship This requirement for a particular arrangement was the basis of the ideas first formulated earlier by Schmidt and his colleagues,¹¹ when they outlined the principles of topochemical reactions in organic solids

In certain crystals non-reactivity is understood as arising either because the reaction centres are too far apart or because the required symmetry relationship is absent. Indeed, where reactivity under inappropriate circumstances has occurred, the reaction has frequently been considered to occur at certain crystalline imperfections.

It might usefully be asked, therefore, what is the flexibility in the parameters defining the geometry of a reactive double-bond configuration?

A system which has thrown considerable light on this question has been described by Theocharis *et al.* using dibenzylidenecyclopentanone as the parent compound¹⁶

DBCP crystallises in the space group $C22_1$ with cell parameters of $a = 11\ 803(2)$, $b = 5\ 698(4)$ and $c = 20\ 872(2)\text{\AA}$, there are 4 molecules per unit cell. The molecules are arranged in stacks along $[010]$ —see Fig. 5—in such a way that nearest neighbour molecules are related by translation along $[010]$, such that $C(2)$. $C(13')$ is $3\ 714(5)$ and $C(6)$. $C(5')$ is $3\ 725\text{\AA}$, the primes indicate symmetry related molecules. The dimer obtained from the solid state reaction packs into the tetragonal space group $P4_12_12$ with $a = b = 10\ 860$ and $c = 23.979\text{\AA}$, $z = 4$.

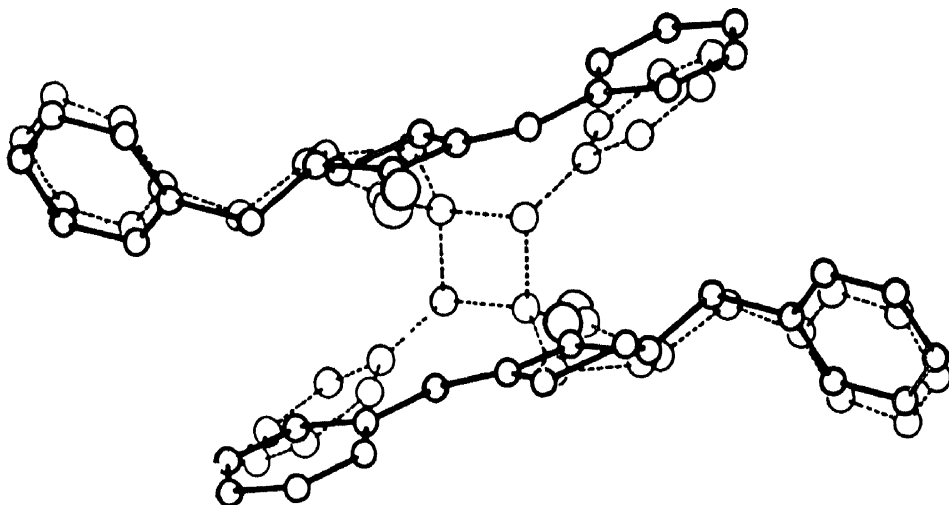


FIG 4 Composite diagram of 'incipient' dimer and 'product' dimer illustrating the relative positions of the monomer and dimer molecules

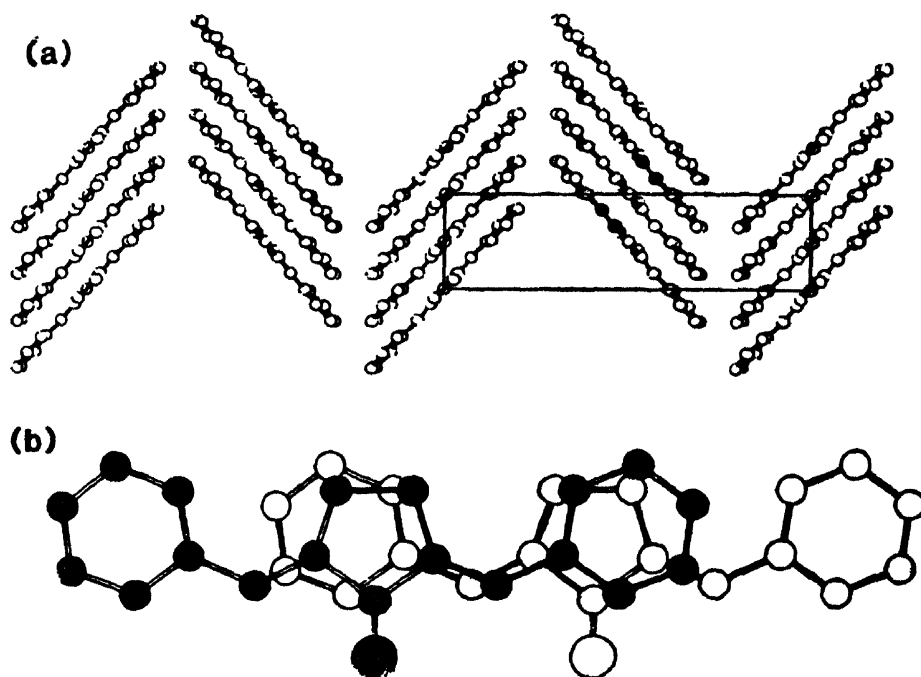


FIG 5 (a) DBCP structure viewed along the *a*-axis (b) A view along a direction perpendicular to the mean molecular plane of the 'incipient' dimer pair; the angle between the reactive is 56°

Close inspection of the monomer structure reveals that the two bonds which react to give the cyclobutane ring belong to benzyl groups which are parallel, but not themselves colinear, there is a rotation of 56° between them. It is argued that although this is not the geometry generally considered conducive for a topochemical reaction, given that the mean distance separating the potentially reactive centres is well within the limits previously deduced to be necessary for such reactions, upon photoexcitation, there is sufficient overlap and interaction of the p_z -orbitals of the double bonds involved in the reaction, for reaction to occur.

In the case of DBCP—and in contrast to BBCP—reaction yields an amorphous product. This most likely results from the intrinsic rigidity of the rather large molecular framework, with the product dimer not being readily accommodated within the monomer lattice.

Other photo-induced phase transformations have been observed. For example, the solid-state photochemical behaviour of trans-stilbenes has long been of interest and in particular the fact that, in contrast to the cinnamic acids, when crystals of the parent material are irradiated with u.v. light *cis-trans* isomerization occurs without [2 + 2] cycloaddition of the exocyclic double bond. When the dichloro derivative is irradiated, however, reaction ensues¹⁷. The *p*-methoxy derivative was studied because there was some possibility that the methoxy group might "steer", see later, the structure into a reactive arrangement, and indeed irradiation of single crystals resulted in significant changes in the infra-red pattern.

Further study, however, confirmed that no chemical reaction had occurred, but rather that a novel photoinduced phase change had taken place with substantial changes in molecular conformation.¹⁸ *p*-Methoxy stilbene packs in the space-group $Pbca$, the asymmetric unit comprising half the molecule; the centre of the exocyclic double bond is located on a crystallographic centre of symmetry and the molecule is flat. The view along the *c*-axis of the crystal structure is shown in Fig (6a). Irradiation of a single crystal results in a change in space group, but significantly the single crystal character of the specimen is retained.

The irradiated material packs in the space group $P2_1/n$. Within the asymmetric unit the methyl carbon, as well as part of the phenyl group were refined at two different positions, each with a refined occupancy of 0.5. The carbon atoms of the phenyl group bonded to the two substituents (double bond and methoxy), the oxygen, and the double bond carbon refined to a single position. Rotation around the single bonds linking the double bonds to the phenyl rings resulted in a structure which was no longer planar, Fig 6(b).

The transformation has been suggested to take place through an excimeric intermediate. Ordinarily the excimer may relax back to the ground state allowing the

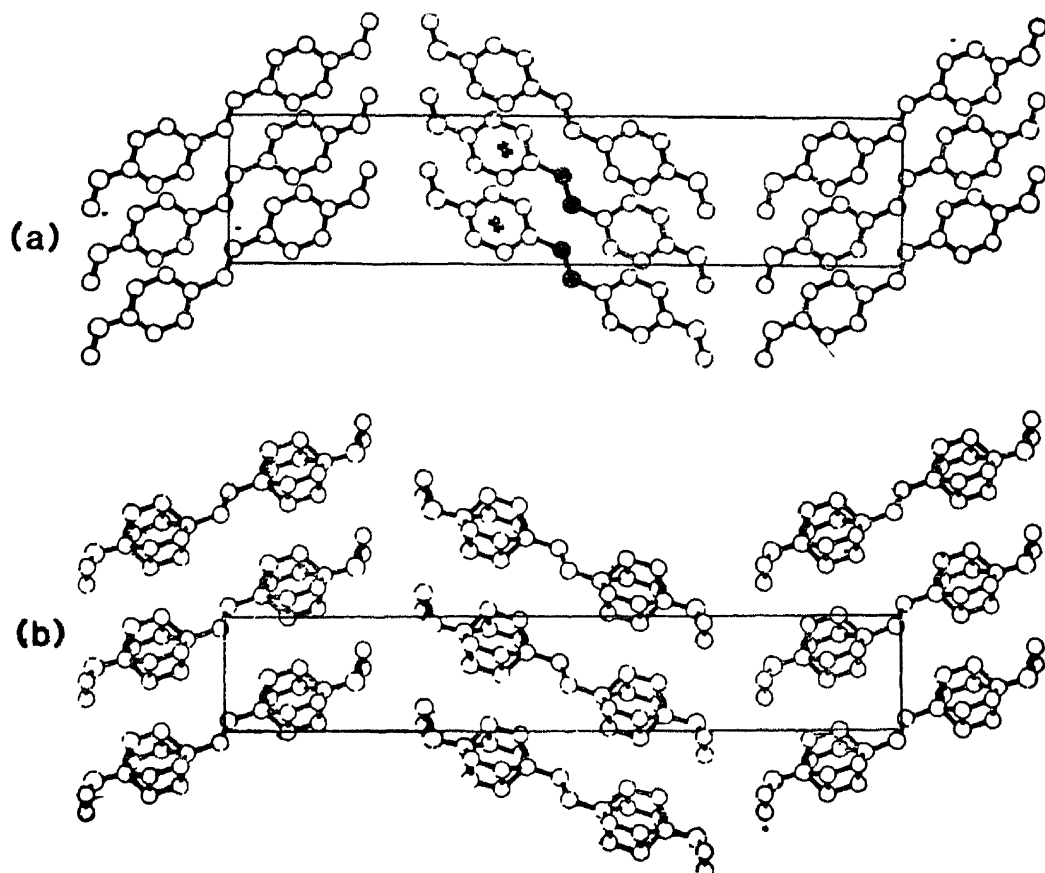


FIG 6 (a) Crystal structure of *p*-methoxystilbene viewed along the *c*-axis (b) After irradiation of a single crystal the centre of the exocyclic double bond coincides with a crystallographic centre of symmetry. The phenyl rings adopt two positions within the crystal—see text.

constituent monomers to revert to their original positions. Because of the rather crowded nature of the packing in this case, however, it seems that this may not be possible and instead the ground state molecules take up new positions resulting in a new structure. It is noteworthy that the whole process is however accommodated within the single crystal structure.

2 RECENT TRENDS AND DEVELOPMENTS IN CRYSTAL ENGINEERING

Crystal engineering, a concept¹¹ first introduced to organic solids by Schmidt in 1971, still generates considerable interest and study. Ideally it may be considered as the deliberate modification of a molecule by, for example, the addition of specific functional groups, such that packing into a desired crystallographic array occurs. As a consequence, the solid state properties of the crystal, including solid-state reactivity, may be controlled. Specific pair interactions which have been identified include $C=O \cdots Cl$, $C=O \cdots Ph$ and $Cl \cdots Cl$, and in general the identification of dominant interactions within a series of compounds requires a systematic study in which gradual changes in molecular structure are made^{12,13}

One previously held view was that chloro-methyl interchange is possible. Consideration of Table I reveals that the pClBBCP and pMeBBCP derivatives are isostructural, as indeed are the BpClBCP and BpMeBCP derivatives. It was expected therefore that both groups of compounds should be capable of forming solid solutions of varying composition, with isotonic changes in cell parameters and melting points. Such was indeed the case.

Interestingly, however, this strict chloro-methyl interchange does not exist for the compounds pClBpBrBCP and pMeBpBrBCP. The principal differences in molecular structure may be appreciated from an examination of the structures projected along, approximately, the C(2)–C(6) bond, see Fig. 7. The pMeBpBrBCP derivative, which is photoactive, has an essentially linear geometry whilst the stable modification of pClBpBrBCP consists of molecules with a substantially 'bent' geometry.¹⁹ The nature of the interactions in these and similar crystals which gives rise to this rather pronounced change in geometry has been investigated using semi-empirical methods as well as more quantitative methods.^{20,21}

The idea of structural mimicry—whereby a molecule may be induced to adopt a new conformation different to the one it adopts in its own pure lattice—has been explored using these derivatives. Theocharis *et al.* have shown, see Fig. 7, that when mixed crystals of pClBpBrBCP and pMeBpBrBCP are grown the conformation taken by the pClBpBrBCP derivative is very similar to that of pMeBpBrBCP, and that both components are able to react.²²

3. MORPHOLOGY CONTROL AND THE DETERMINATION OF ABSOLUTE CONFIGURATION

In the context of generating optically active product from a solid state reaction—see reference 23 for full details of the ways in which this may be achieved—a key question

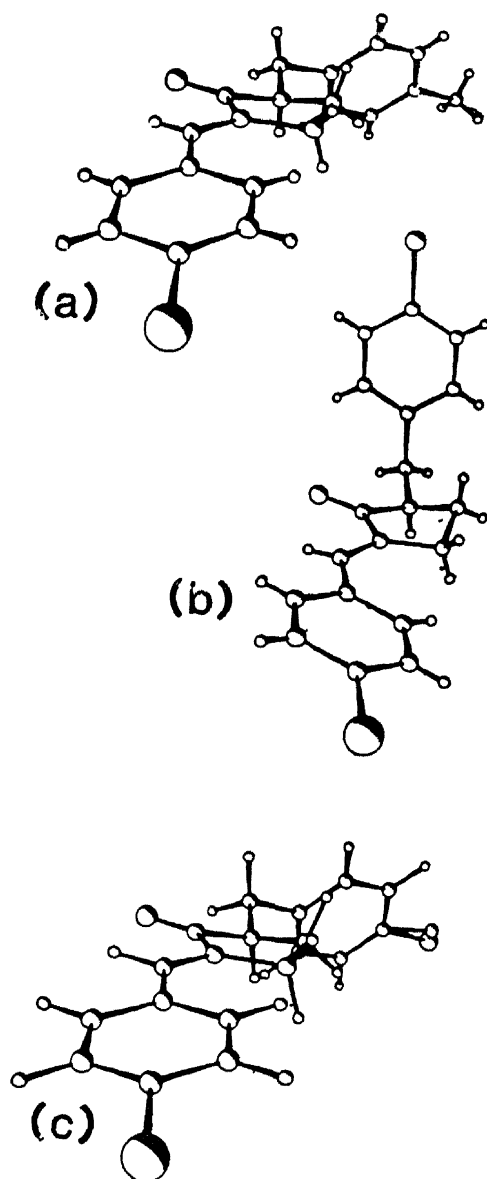


FIG 7 Molecular conformations viewed approximately along the C(2)-C(6) bond for (a) pMeBpBrBCP, (b) pClBpBrBCP and (c) mixed crystal of pMeBpBrBCP and pClBpBrBCP. In the latter case the chloro-derivative adopts a very similar conformation to that of the methyl-derivative

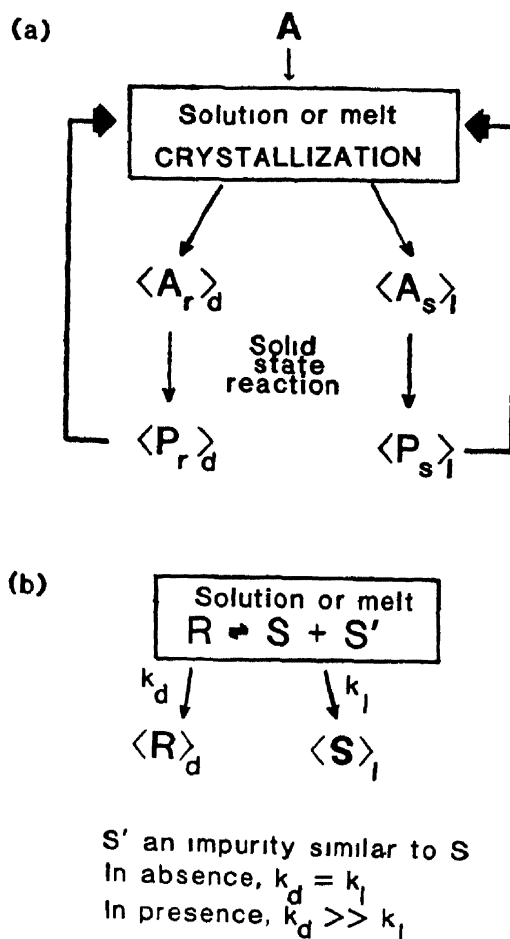


FIG 8(a) Amplification of subsequent product chirality as a result of feedback from addition of initial product. The "inversion rule" relates to the fact that, as shown in the lower part of the figure, crystals of opposite handedness are produced. A = reactants and P = products. (b) Spontaneous crystallization to give a $\langle R \rangle_d$ and $\langle S \rangle_l$ conglomerate, with the growth of $\langle S \rangle_l$ crystals being retarded as a result of the presence of S' impurity—see text.^{37, 24, 25}

is whether significant activity may be obtained from a single crystal reaction. In general it would be advantageous if the generation step which introduces asymmetry could be followed by an efficient feedback mechanism.

Green and Heller²⁴ proposed a cyclic process, see Fig. 8, in which the products of the solid state reaction might, by incorporation into the melt or the solution, drive the crystallization step preferentially towards one of the two enantiomorphous phases.

The proposal was tested using the reaction of bromine and 4, 4'-dimethylchalcone—a gas solid reaction which yields a slight excess of optically active product when a single crystal of the chalcone is used; see Fig. 9. It transpires, however, that in such an experiment the product obtained from a crystal of, say, right handed character repeatedly caused preferential crystallization of the reagent into a crystal of the left-handed form. The term “inversion rule” was coined to describe this effect.²⁵ The explanation rests in the selective adsorption of small amounts of impurities at the growing sites of a specific face of a crystal,²⁶ with this adsorption drastically reducing the relative growth of this particular face with respect to other faces of the same crystal. Two consequences are foreseen: firstly, a decrease in the overall growth rate, Fig 8(b), and secondly, a pronounced change in crystal morphology.²⁵ Lahav, Leiserowitz and their co-workers have now demonstrated that numerous examples of enhanced growth of selected configurations in the presence of impurities could be expected using this approach. When (R, S)-threonine is crystallised in the presence of various impurities (typically 900mg of threonine and 100mg

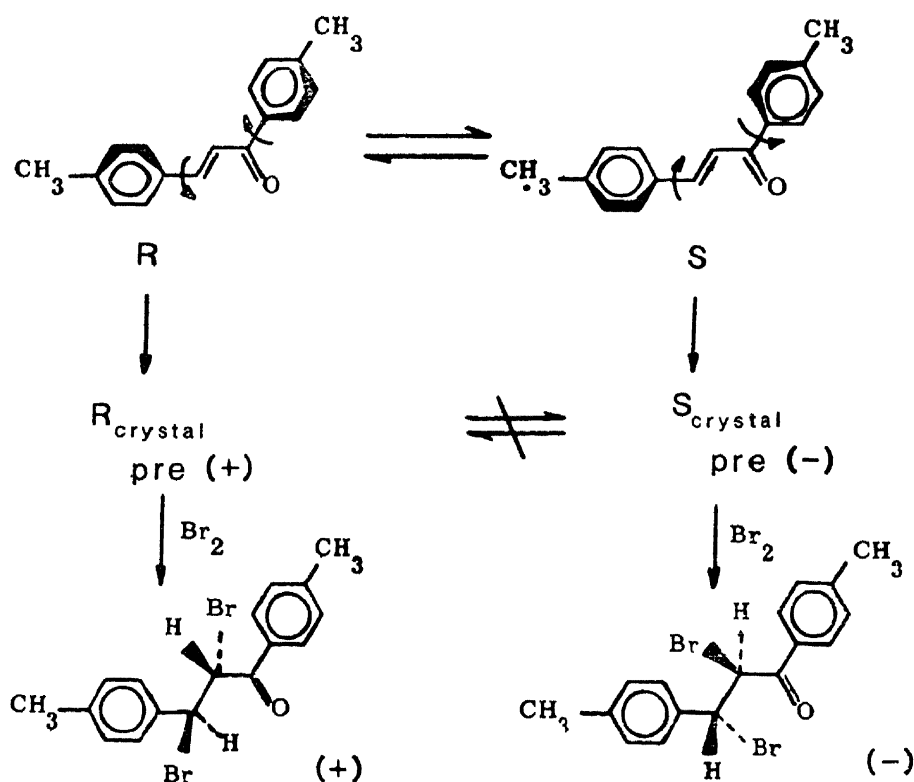


FIG 9 Schematic diagram of the bromination of crystals of dimethylchalcone (with crystallizes into the space group $P2_12_12_1$) illustrating how either (+) or (−) dibromide may result from the reaction of a single crystal²⁴

impurity), the event of the enantiomeric excess within the first crop of crystals is, in some cases, in excess of 95 per cent. Furthermore, in extending their work to amino acids and related materials a particularly important aspect of this selective adsorption has been developed ²⁷

These observations may be viewed in a different way and the question asked as to whether it is possible, knowing the absolute configuration of the material produced in enantiomeric excess, to determine the absolute configuration of the additive molecule. The answer is a resounding yes, and several examples have now appeared which demonstrate this important extension ²⁸

Consider the case of a polar crystal. We may schematically represent the arrangement of the molecules within the crystal as shown in Fig 10. The unique axis of the crystal is parallel to the $X-A$ molecular axis. Impurity molecules of the type $X-Y$ will be accepted at f_1 and f_2 ; but not at f_3 , f_4 or f_5 . The adsorption will then lead to retarded growth along one direction of the crystal and either an increase in area of the inhibited faces with respect to the unaffected ones, or to the development of new faces on the affected side of the crystal

In principle it should be possible to determine on which of the polar faces the impurity has been adsorbed, and hence determine the absolute chirality of the crystal. This has been demonstrated, for example, for enantiomerically pure *tr*-cinnamoyl-*(S)*-alanine which crystallizes in the polar space group $P2_1$. The principal question upon which the assignment of an absolute configuration rests is whether the $-OH$ groups of the acid point along $-b$ or $+b$; once this is known the configuration is known ²⁸. This question of orientation may be answered if, by selective adsorption, the orientation of the particular functional groups within the polar crystal with respect to the crystal axis is determined

Indeed this method is not limited to polar crystals, but has been applied to effect morphological changes in achiral crystals composed of, for example, racemic mixtures ³. Whilst X-ray analysis will not distinguish between the enantiomeric crystal structures $\langle R \rangle$ and $\langle S \rangle$, it establishes unambiguously the sites occupied by the R and S moieties with respect to the crystal axis in the centrosymmetric crystal. If the structural information contained in the racemic crystal is transferred to a third chiral molecule interacting stereospecifically with the racemic system through

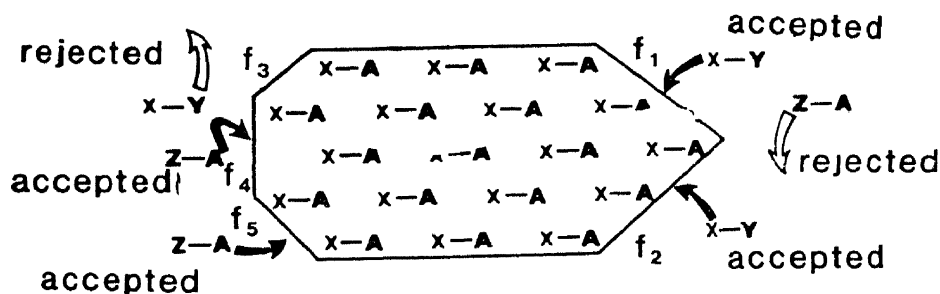


FIG 10 Rejection and acceptance of specific molecules at the different faces of a polar crystal—after Addadi *et al* ³

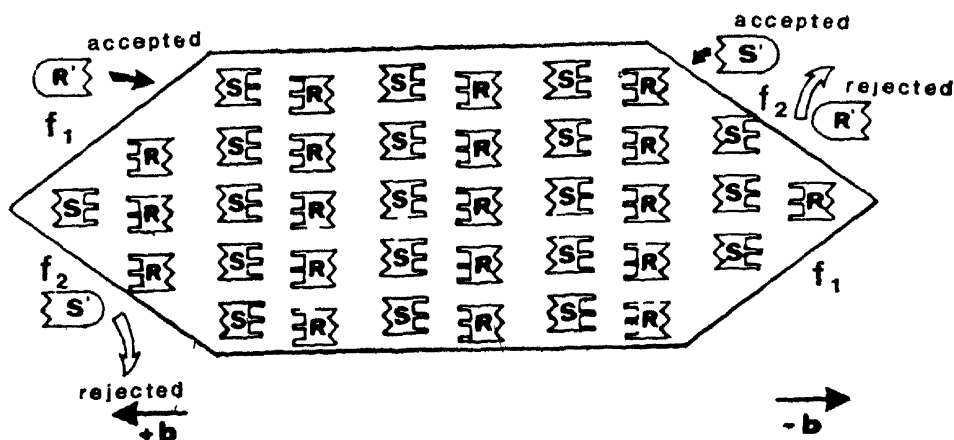


FIG 11 Schematic illustration of how chiral molecules may induce changes in the morphology of a centrosymmetric crystal, composed of a racemic mixture—after Addadi *et al.*³

a well-defined mechanism, then the absolute configuration of the resolved impurities may be obtained, Fig. 11

The importance of this point can be best appreciated when it is realised that until 1951, (when the utilization of the anomalous dispersion of X-rays by J M Bijvoet was first used) the assignment of an absolute configuration to a molecule was not possible—and to this date the method of anomalous dispersion remains in isolation

4 POLYMERIZATION OF DIACETYLENES

There is considerable interest in developing conjugated organic polymers which may be made conducting upon doping with various electron donor or acceptor compounds. To date success has been achieved with systems of the type polyacetylene, polyphenyl and polypyrrole.²⁹

Diacetylene derivatives³⁰ represent an important group of materials with interesting electrical properties. They also represent an important class of materials for which the monomer phase acts as a three-dimensional template for the growth of polymer product. This 1,4-addition reaction, where polymerization occurs in the solid state as a result of successive tilting of monomer molecules, allows the synthesis of fully conjugated essentially defect-free crystalline polymer of high molecular weight. Large single crystals of conjugated polymer, as a result of topochemical polymerization, may result. In general, however, the polydiacetylenes are insulators and the conversion to conducting material has not been possible by normal doping methods. Such is generally not the case for less well ordered samples e.g. multilayer samples, where iodine doping has resulted in conductivities approaching 10^{-6} S/cm.

Recently, however, Nakanishi and his colleagues³¹ have attempted to prepare a doped monomer crystal such that the dopant is locked into the lattice during polymerization, see Fig 12, and it is of interest in these systems to know where the

dopant is located—both in the monomer and in the polymer. This would allow a greater understanding of the nature of the dopant-organic interaction which governs the conductivity of the polymer.

Theocharis *et al.*³² have obtained structural data on a *p*-toluene-sulphonate diacetylene derivative in which the dopant was AgClO_4 . The tosyl derivative was chosen for a variety of reasons, particularly that the incorporation of sufficient dopant does not result in a new polymorph or hinder the polymerization process. It is also an advantage that the material—unlike many diacetylenes—is not readily polymerized by the X-ray beam. The unit cell of the doped and pure diacetylenes are very similar so that polymerization proceeds in the normal manner. Fig. 13 illustrates the molecular structure of the perchlorate doped *p*-TS. The Ag^+ is located—as expected—near an electron rich part of the sidechain.

5 REACTIVITY IN INCLUSION COMPOUNDS AND ZEOLITE MATRICES

The photodecomposition of alkanones included within urea complexes has been studied by Casal *et al.*³³ Urea, when crystallized in the hexagonal lattice, possesses long channels of approximately $5\text{\AA}$ diameter into which guest molecules are incorporated. For 5-nonanone the possible reactions which may occur are shown in Fig. 14. In solution photodecomposition occurs principally via the Norrish Type II reaction, leading to 2-hexanone, propylene and two isomeric cyclobutanols, *see* scheme. The crystalline hexagonal urea complex gave, on the other hand, essentially only one cyclobutanol isomer—the *cis*. The formation of the *cis* isomer may be rationalised in so far as formation of this product requires less stringent rotational requirements. The generation of the cyclobutanol occurs without significant loss of integrity of the crystal lattice.

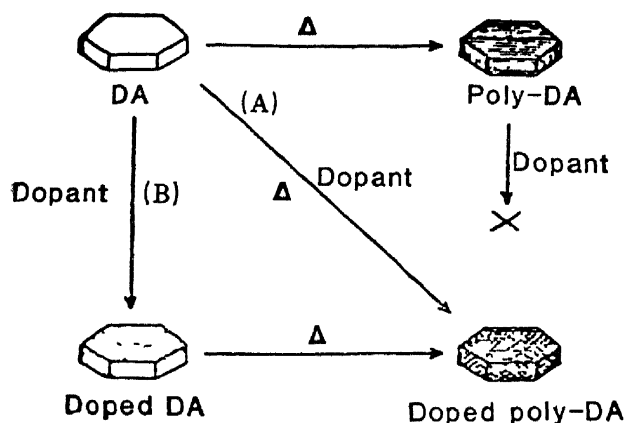


FIG 12 Schematic illustration of two approaches to the production of conducting polymer crystals. Path (A) involves polymerization in an atmosphere of dopant whilst path (B) requires the growth of monomer crystals *containing* dopant molecules. For the case of (B) the dopant molecules should not modify the usual packing arrangement of the monomeric material. after Nakashii *et al.*³¹

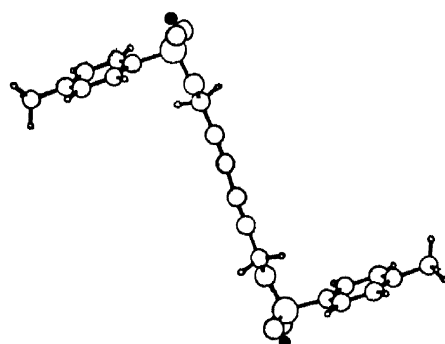


FIG 13 Molecular structure of the hexadiynylene toluene-*p*-sulphonate (*p*TS). The filled circles represent the position of the Ag^+ component of the AgClO_4 dopant.

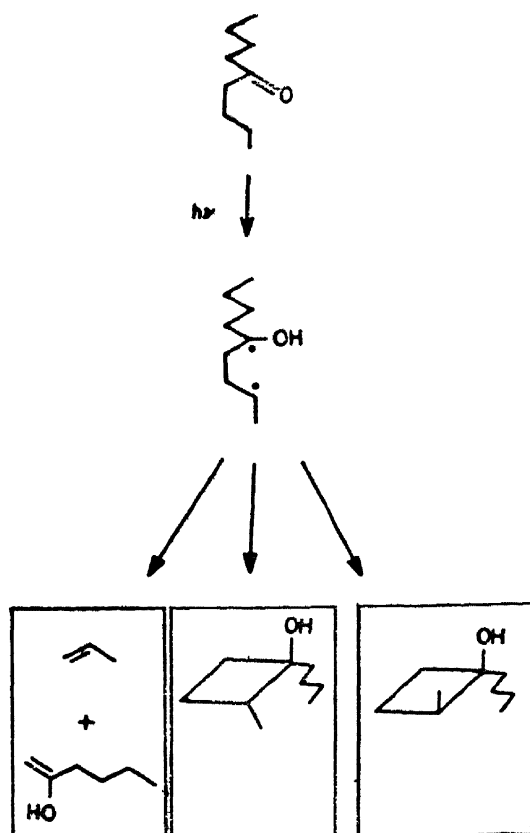


FIG 14 Schematic illustration of the possible reactions—via the Norrish Type II reaction—of 5-nonanone—after Casal *et al*³²

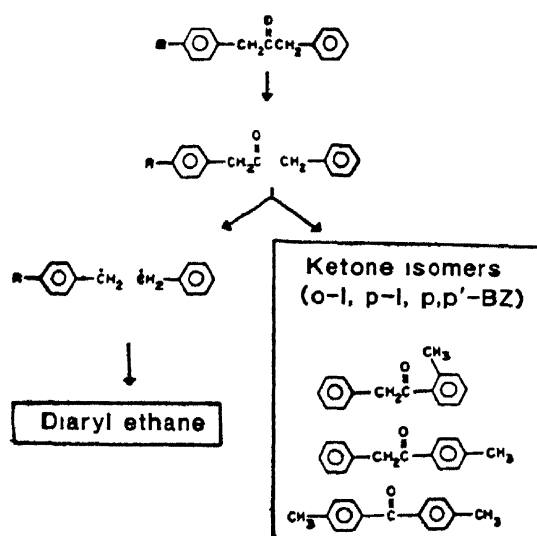


FIG 15 Possible photolysis steps for dibenzylketone (DBK) and *p*-methyldibenzylketone ($R = \text{CH}_3$).

When dibenzylketones are adsorbed on to zeolitic materials⁷ the products which are obtained upon photolysis are very sensitive to both zeolite structure and to the presence of adsorbed additives, such as water, benzene, cyclohexane and hexane. For example in the case of dibenzylketone (DBK) and its *p*-methyl derivative (pMeDBK) the possible photolysis steps are shown in Fig. 15. In zeolite Na-A, where the entrance pores are too small (ca 4 Å) to allow entry of DBK or pMeDBK into the cavities, the products of photolysis are completely analogous to those from reaction in a homogeneous solution. In thoroughly dehydrated Na-X or -Y, however, where the pore openings are ca 8 Å in diameter the yields of DPE* are 60 and 85 per cent, respectively for pMeDBK the corresponding values are 18 and 19 per cent. When exposed to benzene vapour the yield of DPE is only 37 per cent for Na-Y, with isomers of DBK becoming the major products. When water is added to Na-Y only traces of isomers were observed.

It appears that the additives shroud the walls of the zeolite, thus presenting a rather more confined volume in which decomposition may take place, Fig. 16. The restricted motion then leads to an increased cage effect, with enhanced recombination of the generated radicals.³⁴

*Diphenylethane

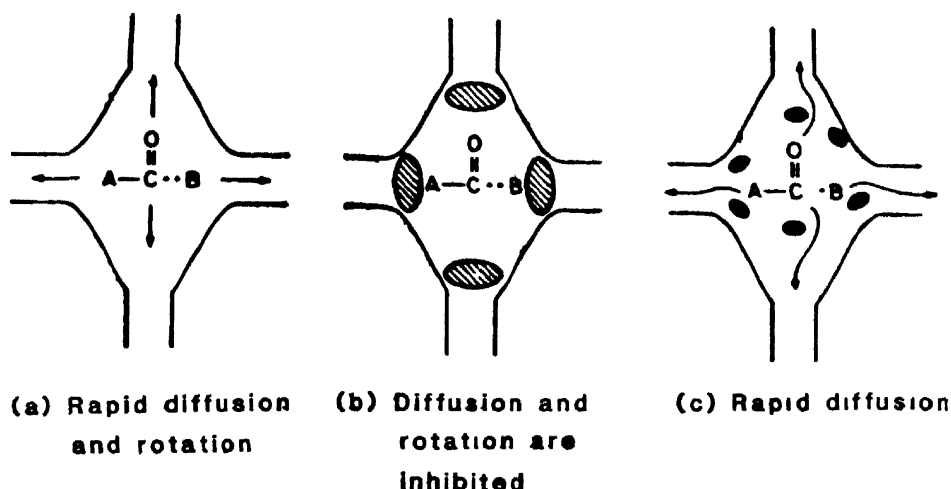


FIG 16 Schematic illustration of the influence of secondary guest molecules upon the reaction of primary radical pairs. Without additives (case (a)) there is rapid diffusion and rotation of the radicals. When an organic reagent is present (case (b)) it is postulated that both diffusion and rotation are inhibited, whilst in case (c) water modifies the rotation but not the diffusion of the radicals—after Turro *et al*.⁷

Adsorption of molecules onto other types of surfaces has also been investigated with a view to modifying reactivity. Thus photocatalysed olefin *cis-trans* isomerization has been observed for substituted styrenes³⁵ when exposed to the semiconducting material CdS and subsequently excited by light of wavelength shorter than its band gap of 2.4eV, approximately 520nm. A possible mechanism for the reaction is that electron transfer from the olefin to the photogenerated 'hole' in the semiconductor occurs, with the generation of a radical-cation. When dianthracene is adsorbed, the CdS serves as a heterogeneous photocatalyst for monomerization.³⁵ When the dimer is irradiated in methylene chloride with light of wavelength greater than 450nm no monomerization takes place. In the presence of CdS anthracene results in high yield.

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CRYSTAL ENGINEERING AND CHEMICAL REACTIVITY OF ORGANIC MOLECULAR SOLIDS*

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Organic solid state chemistry is a field which lies at the crossroads of solid state science, organic chemistry, structural chemistry and X-ray crystallography. In general, it is concerned with the ways in which organic molecules pack in crystals. Reactions which are controlled by the manner of packing are termed topochemical and some recent extensions to the topochemical principles are discussed. In order to systematise the subject, however, a predictive control over structure is required and this leads to the concept of crystal engineering which has been illustrated by the importance of secondary molecular motifs. A better ability in manipulating crystal structures implies that more reliable values for non-bonded atom potentials are becoming available. This information can in turn be employed to carry out crystallography with packing or real-space considerations. It is clear that there are several applications of crystal dissymmetry to academic and practical questions. The chirality of a crystal structure may be exploited in asymmetric synthesis, determination of absolute configuration and in the choice of materials for non-linear optics. Organic solid state chemistry is also related to the design of organic metals and a clear understanding of packing can only result in more deliberate searches for new molecular conductors and superconductors.

Key Words : Organic Solid State; Topochemistry; Crystal Engineering; Real-Space Crystallography, Organic Metals

INTRODUCTION

THE twentyfirst and final chapter of a recent monograph¹ on solid state chemistry begins thus: "This book could not be concluded without at least some mention of organic materials. Usually the fact that many organic substances are solids at room temperature has little bearing on their chemistry." Notwithstanding the apologetic tone of this quotation and the empirical origins of organic solid state chemistry (OSSC), the present article will attempt to show that progress in the last few years has hinted at exciting possibilities for this latest addition to the discipline of solid state chemistry.

Research in OSSC today has important implications in diverse areas of chemical research. Using the principles of OSSC, one may for instance monitor organic reactivity at the molecular level, answer stereochemical questions of a fundamental nature, carry out novel organic transformations and study various ways in which

organic molecules organise themselves, be they in a crystalline solid, a nematic mesophase, a polymer, a film or a micelle. Impetus to research in OSSC also stems from the fact that such work may lead to the development of molecular materials which are important for electronics and communications applications. Chemical memory devices, organic conductors and frequency doublers are not yet commercial products while a high temperature organic superconductor may remain a dream for some time to come. But all these represent worthwhile goals to strive towards since a substantial amount of new chemistry and an improved understanding of structural principles is bound to emerge in such a quest.

At the very outset one must be aware that there are notable differences in the methods employed in the practice of OSSC when compared to the solid state chemistry of non-molecular materials. The physical and chemical properties of organic substances are such that the standard techniques of preparation and characterisation of inorganic materials may be of only marginal utility. Spectroscopy, in the bulk and on surfaces, and microscopy, both optical and electron, are vital tools of modern solid state chemistry. These techniques have, however, not been generally adapted to OSSC. In many cases, even suitable methods of purification have not been standardised. The traditional token of purity for solution organic chemists, that is ± 0.3 per cent variation from the calculated C, H and N elemental analyses, is clearly inappropriate in many solid state studies!

Since OSSC is still in the descriptive phase with occasional forays into the realms of correlation and prediction, X-ray crystallography occupies a central position in this subject. It is the most common way of determining molecular and, more importantly, crystal structures of organic molecular solids. Many categories of organic solid state reactions are governed by the crystal structure of the reactant and determining the structure of this reactant assembly of molecules is a *sine qua non* to rationalising solid state reaction mechanisms or to acquiring a body of information that is representative enough to make considered structural predictions. X-ray crystallography will therefore continue to remain very important to OSSC and this situation is unlikely to change in the near future as there is yet no definitive answer to the question "Can one reliably predict the crystal structure of an organic solid?"

The issue of structure is a principal one in OSSC, as indeed it is in all branches of solid state chemistry.² Generally, an understanding of structural concepts may be utilised in two distinct ways to carry out novel chemical reactions and to devise new materials with specific physical properties, be they optical, electronic or mechanical. In this article, some significant recent developments in OSSC and some potentially important prospects for the future are highlighted. Almost all these areas are concerned with obtaining, understanding or exploiting the crystal structure of an organic compound.

TOPOCHEMISTRY AND THE PREDICTION OF SOLID STATE REACTIVITY

The work of Gerhardt Schmidt and his co-workers is of such seminal importance to OSSC that, more than twenty years after its publication^{3,4,5} it still remains the

inevitable starting point for reviews in the field⁶⁻¹⁵ Though early work on the photodimerisation of crystalline olefins to give cyclobutanes had been reported,¹⁶⁻¹⁸ Schmidt was the first to be able to correlate a large number of seemingly unrelated chemical and crystallographic facts and in doing so to lay the foundations of OSSC.

Schmidt found that for many photodimerisable olefins, the molecular packing plays a crucial role in determining the course and outcome of the solid state reaction. These reactions are termed topochemical¹⁹ since they are considered to occur with a minimum of atomic or molecular movement. Since any molecular diffusion of the conventional type is precluded in the solid state, such topochemical reactions have also been termed 'diffusionless'.²⁰ In a topochemical situation, reaction only takes place if the geometry of the molecules in the reactant crystal permits it. Conversely, no reaction occurs if the geometry of the adjacent molecules in the crystal is inappropriate. As a corollary, the topochemical principle, as stated above, also implies that the structure of a product of such a reaction bears a close relationship to the crystal structure of the reactant. Because of this fact, there are a very small number of products in the typical topochemical reaction.

These features were illustrated by Schmidt with reference to the *trans*-cinnamic acids. These compounds crystallise in one or more of three structural types α , β and γ . While the α -acids have short crystallographic axes greater than $5.2 \text{ \AA}$, the β -acids are characterised by short axes of ca. $4.0 \text{ \AA}$. Fig. 1 shows that in both these cases, 'potentially reactive' double bonds are parallel and approximately $4.0 \text{ \AA}$ apart when measured from bond centre-to-centre. In the case of the γ -acids, however, the short axes are around $4.7 \text{ \AA}$ with the result that nearest parallel double bonds are at this increased separation. These crystallographic observations when coupled

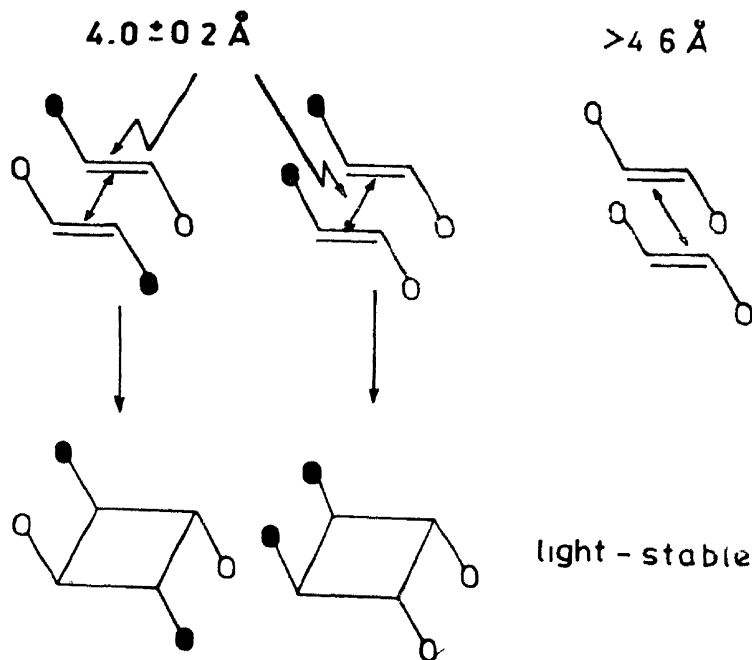


FIG. 1 Photoactive (α , β) photostable (γ) forms of *trans*-cinnamic acid

with the photoreactivity of the α - and β -forms and with the photostability of the γ -form lead to a formulation of the topochemical rules for the $2 + 2$ photodimerisation of olefins —

(1) The solid state reaction only occurs if the double bonds are closer than some 'threshold' separation which lies between 4.0 and 4.7 Å (Schmidt used a value of 4.2 Å for this cut-off).

(2) The crystal symmetry of the reactant transforms as the molecular symmetry of the product.

Several examples of solid state photodimerisation reactions which obey these rules have been described.²¹ While Schmidt extended the topochemical argument to aliphatic unsaturated acid derivatives,²² and to quinones,²³ Thomas and co-workers have found that in the 2-benzyl-5-benzylidenecyclopentanone (BBCP) class of compounds, solid state dimerisation is not only topochemical but also topotactic with 'potentially reactive' double bonds being related by a centre of inversion in the reactant crystal.^{20,24-26} The solid state photodimerisation of 3-methyl-4-nitro-5-styrylisoxazole,²⁷ thymine²⁸ and α -benzylidene- γ -butyrolactone^{29,30} have all been found to be topochemical as defined above (Fig 2).

However, other solid state photodimerisations have been described where the reacting double bonds are non-parallel. A notable case is 2,5-dibenzylidenecyclopentanone where the angle between the two reacting bonds is nearly 56°.³¹ Another definitive example is 1,4-dicinnamoylbenzene which photodimerises to give an unusual δ -truxinic product.^{32,33} Again there are cases such as 2-benzylidene-cyclopentanone where even though parallel double bonds are aligned at less than 4.2 Å

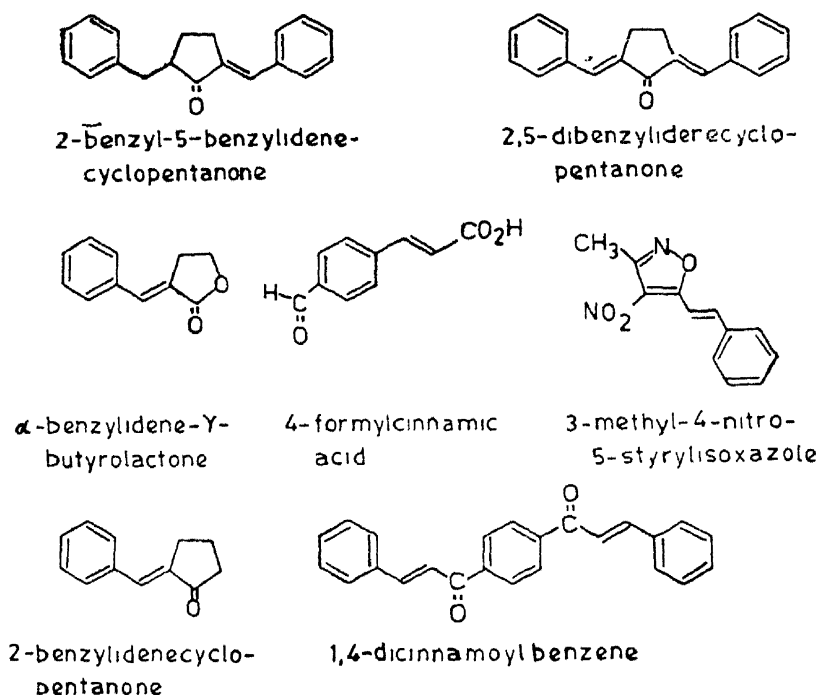


FIG 2

separation, no solid state photoreaction occurs on irradiation³⁰ while in the photo-reactive 4-formylcinnamic acid, a 100 per cent yield of topochemical dimer is obtained even though the reacting double bonds have their centres greater than $4.8\text{\AA}$ apart in the crystal.³⁴

In general, it is chemically unreasonable to expect a 100 per cent correlation between the disposition of point atoms in the solid state and the reactivity which is predominantly an electronic phenomenon. Indeed, it is probably the almost hypnotic fascination for the topochemical rules as formulated by Schmidt (parallel double bonds, distance less than $4.2\text{\AA}$) which, if anything, has led to many of these reactions being considered 'unusual' or 'anomalous'. As early as 1978, it was pointed out that arbitrary geometric criteria could not be used to predict solid state photoreactivity.³⁵ More recently, it has been shown that many of these supposedly anomalous situations may be better understood if orbital overlap rather than double bond centre-to-centre separation is considered.^{36,30} Such an analysis explains the preference for the intermolecular over the intramolecular reaction in 1,1'-trimethylenebis-thymine³⁷ and for the formation of the 7-methoxycoumarin dimer in the solid state.² A simple geometrical argument will show that consideration of both centre-to-centre and plane-to-plane separation of the potentially reactive double bonds is necessary to determine the extent of orbital overlap. Cases like 2-benzylidenecyclopentanone and 4-formylcinnamic acid illustrate the pitfalls of using the centre-to-centre separation alone.

There are yet other situations where a topochemically expected photoproduct is not obtained even though the orbital overlap is favourable. One such case is the 1:1 Donor-Acceptor complex between 3,4-dimethoxy- and 2,4-dinitrocinnamic acids. Here, energy transfer from the $\pi\pi^*$ excited state to an $n\pi^*$ state is facile with efficient intramolecular quenching preventing chemical reaction.^{38,39}

In summary, a classification of these various categories of topochemical processes is attempted in Table I. In *A* and *B*, topochemical and orbital overlap predictions are borne out while in *C*, non-parallel double bonds are considered. In *D*, however, the reaction is formally non-topochemical. Early work⁴⁰ seemed to suggest that such a reaction takes place through defect-controlled energy transfer, but the discovery of metastable phases in anthracene⁴¹ has cast new light on this problem and the possibility of a topochemical reaction proceeding through polymorphs cannot be ruled out. A type *E* process is a seeming violation of the topochemical rules but the anomalies are because of intramolecular energy transfer. These five situations describe all possible combinations of topochemical allowedness or non-allowedness and the presence or lack of solid state reactivity.

Although much work has been carried out on the prediction of topochemical reactivity from geometrical criteria, not much progress has been made in attempting to chart the course of an organic solid state reaction once it has been initiated. The concept of local packing densities has been used to estimate most probable directions for molecular movement during a solid state nucleophilic substitution.⁴³ Crystallographic studies have been carried out on partially reacted photodimerisable

crystals in the benzylbenzylidenecyclopentanone family of compounds.^{41,45} Such studies were possible since the crystallographic unit cells of the reactant and product are virtually identical (Fig 3). These X-ray measurements reveal the positions of unreacted and reacted molecules and, by implication, the direction of movement of molecules towards the transition state for this 'diffusionless' reaction. Theoretical modelling of such transformations should become feasible with the appearance of better and faster computers, and such reactions are possibly easier to handle computationally than their solution counterparts. The next several years will probably see an increased emphasis on the 'dynamics' rather than the 'statics' of an organic solid state reaction.

NOVEL REACTIONS—ORGANIC SYNTHESIS

Although the major application of OSSC is not in the area of organic synthesis, the topochemical principle may be exploited in sequences towards compounds with unusual structures and/or high molecular symmetry. There are several examples where a novel product is obtained in a high yield in a solid state process even though it occurs in reduced yield or not at all in the corresponding solution transformation.⁴⁶⁻⁴⁸ An ingenious example is the eight-centre dimerisation of tetrachlorodibenzylidene acetone to yield a novel tricyclic cyclohexanedione framework.⁴⁹ A

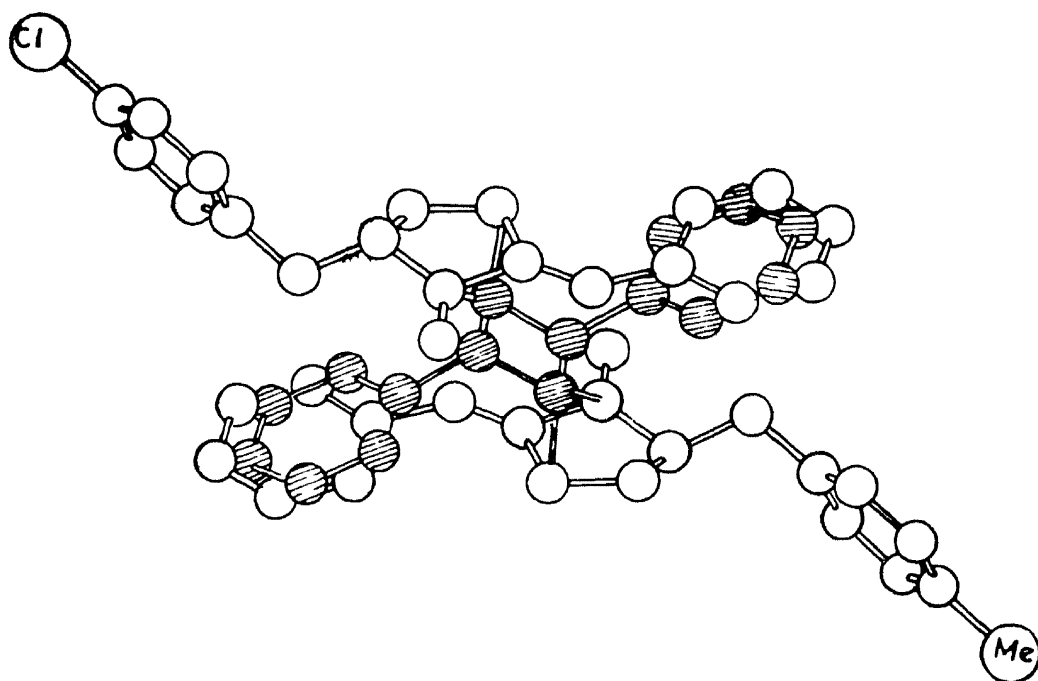


FIG 3 Positions of the monomer (○) and dimer (●) molecules during photoirradiation of mixed crystals of the BBCP's 1 and 2 as determined by *in-situ* X-ray diffractometry on partially reacted single crystals. Notice the formation of the cyclobutane ring and the puckering of the two cyclopentanone residues as the reaction progresses. The atomic positions of the Cl-benzyl and Me-benzyl rings do not change appreciably during the reaction. This 'anchoring' effect is, in large measure, responsible for the single crystal single-crystal nature of the reaction (From Theocharis *et al* 1984)

very real problem with using topochemical reactions in organic synthesis is however, the lack of generality. Much attention in OSSC has been paid to a single reaction, the $2 + 2$ photodimerisation of olefins and not much is known about reactions between two different substances in the solid state, be they photochemical or thermal.^{50,51} An unusual case of a solid state intermolecular Diels-Alder reaction has been reported.⁵² Many solid state intramolecular processes have been described. These include photochemical isomerisation⁵³ and H-atom abstraction.^{54,55} In the latter category, the solid state and solution products are generally different in spite of the reaction being intramolecular and several mechanistic insights have been obtained.

The polymerisation of diacetylene derivatives^{56,57} is an unprecedented solid state transformation where single crystals of monomer are converted to *single crystals* of polymer in quantitative yields. Since there are not many methods of making such perfectly oriented macromolecules, polydiacetylene chemistry has been the subject of extensive investigation. The commercial importance of these materials is obvious. With their highly extended conjugated framework, ease of oxidation, molecular linearity and considerably dichroic character, these substances are potentially very significant for optical and electronic applications. The study of polydiacetylenes doped or otherwise, continues to be one of the more attractive areas of OSSC where collaborative studies between chemists and physicists hold out opportunities for significant breakthroughs.

Another elegant synthetic strategy in OSSC is to use the dissymmetry inherent in a non-centrosymmetric crystal structure to generate molecular optical activity through topochemical reactions. Such reactions were first demonstrated for diaryl-butadiene derivatives⁵⁸ and are illustrated in Fig 4. A compelling reason for interest in such reactions stems from the fact that crystal lattice controlled asymmetric syntheses might well have been involved in the generation of or, at least, in the amplification of optical activity in prebiotic conditions on the earth.⁵⁹ Using these principles, it has been possible to devise a route for an absolute asymmetric synthesis with close to quantitative enantiomeric yield,⁶⁰ while a conceptual route towards pseudo mirror-symmetrical chiral cyclobutanes has been outlined through the device of optimising donor-acceptor interactions in a molecular complex.³⁸

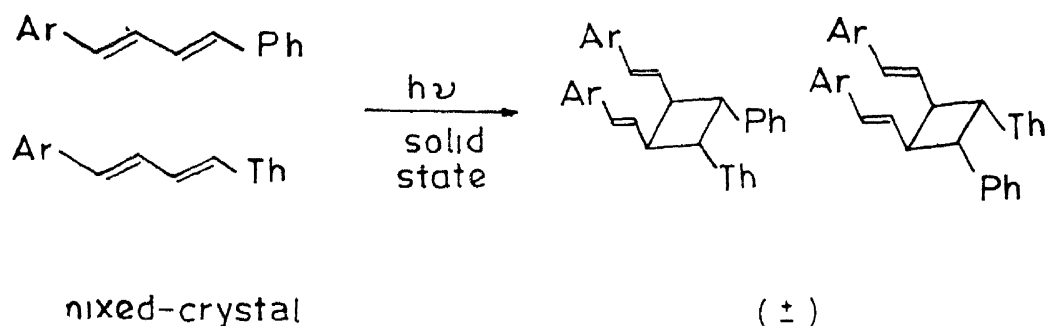


FIG 4 Asymmetric synthesis employing crystal chirality. The mixed crystals of the phenyl (Ph) and thienyl (Th) compounds belong to the non-centrosymmetric space group $P2_12_12_1$ (after Elgaví *et al* 1971)

While it has been recognised that novel organic transformations may be carried out in the interlamellar regions of inorganic layered structures such as montmorillonite clay,⁶⁸ the principles underlying such reactions may be transplanted into the realm of asymmetric synthesis by clathration or enclosure of a potential substrate as a guest material in a chiral host. In this context, a well-studied host material is tri-*ortho*-thymotide, TOT, space group $P3_1$, which shows effective enantiomeric discrimination.⁶¹ A recent report⁶² deals with the oxidation of a prochiral olefin (guest) in the TOT cavity, to yield chiral peroxides in good enantiomeric excesses. Another very effective class of chiral encapsulating materials are the cyclodextrins. For example, α -cyclodextrin and crotonic acid, $\text{CH}_3\text{-CH=CH-CO}_2\text{H}$, form a complex which can be chlorinated in the solid state to yield dichlorobutyric acid, $\text{CH}_3\text{-CHCl-CHCl-CO}_2\text{H}$ in quantitative enantiomeric yield.⁶³

CRYSTAL ENGINEERING AND INTERMOLECULAR INTERACTIONS

Although much structural and chemical data have been correlated on the basis of topochemistry, it was realised^{21,8} that sustained development of OSSC could not be expected unless it was somehow possible to predict crystal structures. The emphasis has been shifting inevitably from the reactions and crystallographic details to predictive exercises. These have proved to be more difficult because an organic crystal structure is the consequence of a balance of many minor and subtle intermolecular forces. In broad terms, a crystal structure of a molecular solid results from a play of dispersive and repulsive interactions^{64,65} and most structures can be somehow painted on this conceptual canvas. However, many alternative structures are seemingly possible within this framework and actually realised in practice as polymorphic modifications. The ultimate choice of a stable molecular packing seems to depend on the relative importance of secondary effects such as coulombic and dipole interactions or weak bonding. These effects all but render transferability of atomic non-bonded potentials impossible in any predictive effort and further they may vary drastically with molecular modifications that are apparently trivial from the solution viewpoint. Realising such facts, it has been the usual practice to study (crystallographically) a series of closely-related compounds so that a common structural principle may be made to emerge. Such activity has been termed crystal engineering.^{21,8}

Crystal engineering is concerned with obtaining topochemical control in systematic ways and with predicting and exploiting crystallisation patterns in organic solids.^{10,66,67,15} By suitable engineering of a family of structures, very specific reaction pathways and products may be obtained repeatedly and reproducibly. The strategy, therefore, involves the choice of molecules according to their shape, size and stereochemistry and then inducing them to crystallise into certain pre-designated crystallographic arrangements. The key to crystal engineering lies in being able to understand the nature of delicate yet non-trivial intermolecular forces.

One of the consequences of Kitaigorodskii's model for the crystal structures of organic compounds is that close-packing is of paramount importance and that

molecules pack in ways such that the 'voids' of one are locked into the 'protrusions' of the other. Volume and shape considerations hold sway rather than electronic factors. Each non-polar substituent of a certain volume can be exchanged for another non-polar group of a similar shape and volume without a change in the crystal structure. Chloro-methyl interchange (volumes Cl, $19\text{\AA}^3$, CH_3 , $24\text{\AA}^3$) is, in fact, well known and a pair of compounds like **1** and **2** is isostructural. As it turns out, each of the individual compounds is photoactive in the solid state and the mixed crystals also react to form pseudoinversion-symmetry cyclobutanes (Fig. 5).

However, volume effects may be used to force the conformations and crystal structures of such compounds into variations. The main difference between the photoactive **3** and the photostable **4** lies in the molecular conformations (Fig. 5). Yet these two compounds will form mixed crystals, isostructural to **3**, primarily as a result of forced changes imposed upon the molecular geometry of the minor component **4** by the major component **3**. In the mixed crystals, the photostable chloro derivative **4** is forced to adopt the molecular conformation, crystal structure and solid state reactivity of the photoactive methyl derivative **3**.^{44,45}

When the crystal structure is defined as a result of optimisation of dispersive and repulsive forces only, such volume effects are likely to be important. The appearance of secondary interactions, however, leads to violations of one type or another from the close-packing principle. It is hardly surprising that the crystal structures of strongly hydrogen bonded compounds depends mostly on the H-bonding requirements. The simplest compounds may adopt the most complex of crystal structures, as for example, hydroquinone (1,4-dihydroxybenzene) or trimesic acid (benzene-1,3,5-tricarboxylic acid). What is noteworthy, however, is the fact that even

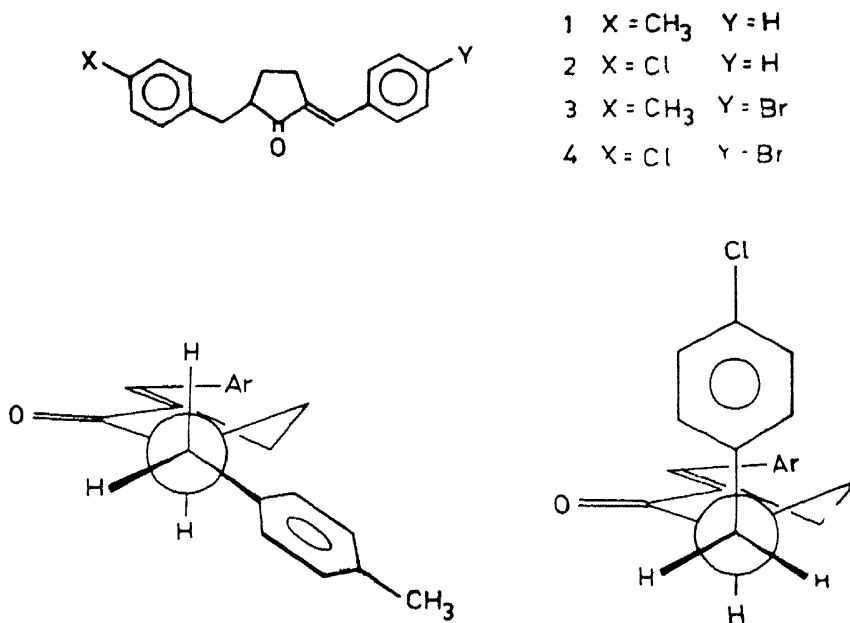


FIG 5 The molecular conformations of the methyl and chloro derivatives **3** and **4** respectively are different as are the crystal structures and solid state reactivity (Ar = $p\text{-Br-C}_6\text{H}_4\text{-}$) (adapted from Jones *et al* 1983)

relatively weak intermolecular forces such as C-H...O, Cl...Cl, C...Cl, C-H...N or S...S may cause deviations from 3-dimensional closepacking. Still, these forces are quite weak and there is a substantial dependence on van der Waals interactions which means that such structures may be understood as gradual perturbations from the Kitaigorodskii model. Substitution of two or more chloro groups on aromatic rings, for instance, leads to preferential adoption of unit cells having a short axis of *ca* 4 Å which is characteristic of a structure made up of highly overlapped molecules stacked with a plane-to-plane separation of around 3.4 Å (van der Waals separation). At least a hundred such chloro compounds are known.^{21,69}

A common feature in the crystal structures of these planar chloro aromatics is the occurrence of a large number of Cl...Cl non-bonded contacts in the 3.2 to 3.6 Å region. These contacts are generally along directions which are parallel to or close to the planes of the aromatic rings, so that molecules which are related by them can be arranged in planar sheet or ribbons. In order then that C...C contacts can be optimised, these sheets can be stacked with an inter-sheet perpendicular distance of 3.4 Å as mentioned above. This kind of structure is illustrated by a compound such as hexachlorobenzene (Fig 6)⁷⁰. Such secondary interactions may also be possible within the framework of stronger forces such as O-H...O H-bonding and a recent analysis of the crystal structures of the dichlorophenols is a representative example.⁷¹

These directional preferences for Cl...Cl interactions have been confirmed in the co-crystallisation of compounds such as 6-chloro-3,4-methylenedioxy cinnamic acid and 2,4-dichlorocinnamic acid as a stoichiometric molecular complex.^{66,69} While specific in-plane Cl...Cl interactions lead to sheet-ordering, the lack of such intermolecular specificity between parallel adjacent molecular sheets leads to a structure which is disordered in the stack direction. It may be shown that such concepts may also be extended to C-H...O interactions and that there is a significant tendency to adopt sheet-based 4 Å structures among compounds which can optimise a large number of such bonds.^{67,72}

A substantial amount of crystallographic information is necessary before reliable structural predictions may be made and it may not always be possible to carry out such a large number of structure determinations for practical reasons. A very

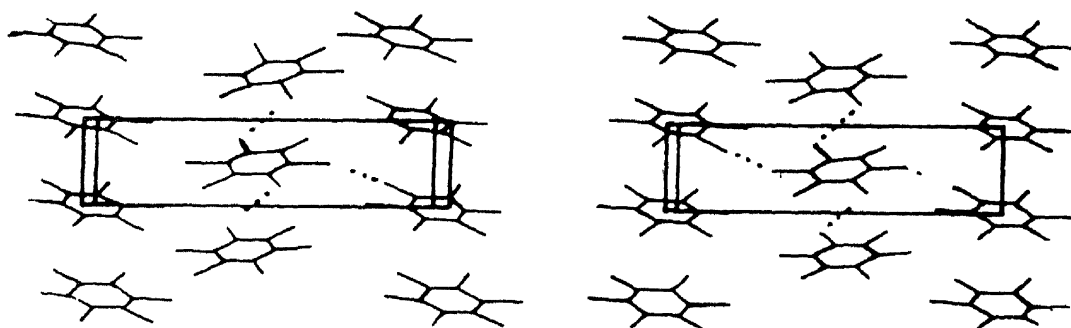


FIG 6 Stereodrawing of the crystal structure of hexachloro-benzene to show molecular ribbons linked by Cl...Cl interactions (after Sarma and Desiraju, 1985)

recent alternative strategy has been to retrieve the desired structural information from the Cambridge crystallographic database ^{73,74} Since organic structures hinge on the manifestation of relatively weak interactions, a valuable insight into the consequences of these interactions, if not their nature, may be obtained by examining an entire family of structures with the database. Several such pioneering studies have appeared in recent years ⁷⁵⁻⁷⁷ Such studies indicate that certain types of intermolecular interactions are associated with only certain geometrical arrangements of patterns or motifs. Hence, approaches through the database may be more fruitful, in this context, than attempting to grapple computationally with weak intermolecular forces.

This section would be incomplete without reference to studies concerning crystal engineering into non-centrosymmetric (NC) space groups. Notwithstanding possible applications in synthesis as outlined earlier, there is considerable interest in obtaining single crystals of organic compounds, which lack a symmetry centre since such crystals would show a non-linear second harmonic generation (SHG) effect upon suitable irradiation. Such molecular materials may be used in the up-conversion in the visible or near UV of powerful IR laser radiation, frequency modulation of a laser beam and for oscillation and amplification in solid state IR-tunable coherent devices. Although early applications have used inorganic materials like quartz, it has been realised that organic compounds have SHG efficiencies that are greater by several orders of magnitude ⁷⁸⁻⁸⁰ A trivial means of ensuring crystallisation in a NC space group is to use a resolved material but such substances are, in general, neither very common nor need they always exhibit good SHG effects.

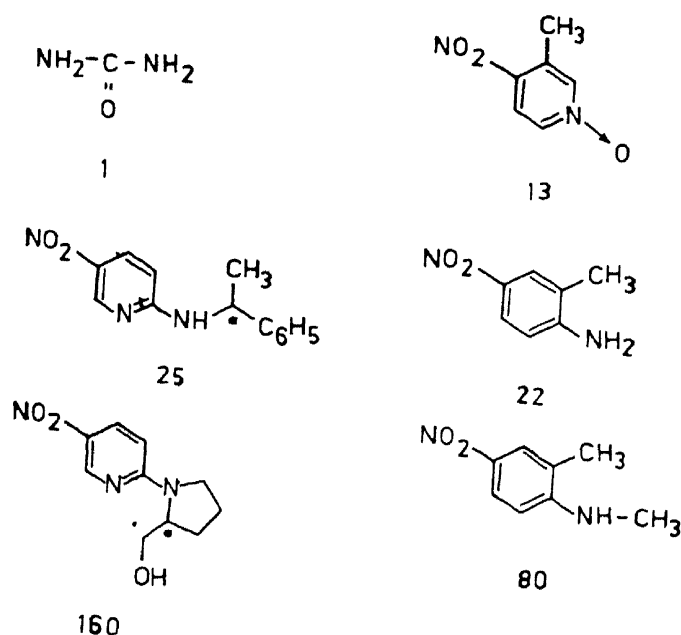


FIG 7 Some organic compounds which show sizable Second Harmonic Generation on laser irradiation. SHG efficiencies are given relative to urea. Asymmetric carbon atoms are marked with an asterisk. Note that only some of these compounds exhibit solution optical activity.

since non-centrosymmetry is a necessary but not a sufficient condition for appreciable SHG. On the other hand, organic compounds which may be electronically suitable for this purpose such as dyes and conjugated polymers rarely adopt NC space groups. Therefore, finding a material for SHG application has been largely a 'hit-and-miss' affair. It is still unknown why some optically inactive molecules resolve spontaneously and pack in enantiomorphous (and therefore, by necessity, NC) space groups. Correlations between molecular structure and the tendency to adopt NC packing are sparse and empirical. For instance, it is reported that, for disubstituted benzenes, the *meta* isomers may have a statistically greater tendency for NC space group adoption than the *ortho* and *para* derivatives⁸¹. The structures of some organic compounds which show large SHG effects are given in Fig. 7. It may be noted that many of them cannot show solution optical activity.

THE ABSOLUTE CONFIGURATION OF CHIRAL MOLECULES

As described above, non-centrosymmetric crystal structures are often packed with enantiomeric molecules. While chemists have recognised the existence of such molecules ever since Pasteur's experiments on hemihedrism in sodium ammonium tartrate in 1848, the philosophical question of how to determine absolute configuration remained unanswered for more than a century till, in 1951, J.M. Bijvoet showed that for a noncentrosymmetric crystal, an X-ray diffraction pattern could be obtained where violations of Friedel's Law ($I_{hkl} \neq I_{\bar{h}\bar{k}\bar{l}}$) could be observed. Using this anomalous dispersion of X-rays, the assignment of absolute configuration was possible.

In recent years, there have been two sets of experiments by organic solid state chemists to determine absolute configuration without using the Bijvoet method. The fundamental concept recognised in both experiments^{82,83} is that any method which fixes the orientation of any functional group of the chiral molecule with respect to the crystallographic axes establishes the absolute configuration of the molecule. These arguments rest on the existence of the polar axis in crystals of chiral molecules. All such molecules must crystallise in enantiomorphous space groups and these have associated with them one or more polar directions. The polar axis is, therefore, a uniquely solid state phenomenon and at a molecular level, its structural implications are that when one views a crystal from the opposite ends of such an axis, chemically distinct parts of the molecules are revealed⁸¹. In the method of Curtin and Paul, a crystal is chosen which exhibits different solid state reactivity at different ends of the polar direction⁸². Gas-solid reactions are convenient for this purpose⁸⁴. These reactivity differences may be monitored through some physical or spectroscopic technique and the direction of a particular functional group is therefore known. From the necessarily chiral morphology of the polar crystal, the sense of the polar axis is also known. A combination of these two facts leads directly to the absolute configuration of the crystalline chiral molecule.

The alternative approach is to monitor changes in the morphology of crystals of pure enantiomer upon the addition of carefully selected impurities. Since crystal morphology depends on the directions of weak intermolecular forces, the presence

of a small amount of an impurity may result in selective absorption on certain faces only, thereby inhibiting further growth on these faces and so effecting gross morphology changes. Since different functional groups emerge at opposite ends of the polar direction, it is possible to design impurities that will be adsorbed selectively at one end only. Observation of the resulting morphology changes establishes a method of fixing the orientation of a certain functional group with respect to the polar axis and therefore of fixing the absolute configuration.⁸³

PACKING CALCULATIONS AND REAL SPACE CRYSTALLOGRAPHY

There are several situations in OSSC where X-ray crystallography is neither possible nor completely reliable. For compounds that are insoluble, unstable, non-volatile or of high molecular weight, obtaining single crystals may in itself be a formidable problem while any attempt at crystal engineering leaves the rhetorical question as to whether polymorphism is important or not in the system under consideration. Finally there are those cases, albeit small in number, where the solution of the phase problem is either ambiguous or intractable with conventional vector space of reciprocal space methods.

In the Kitaigorodskii model, the molecular arrangement in the crystal is based on the intermolecular potential being expressed as a sum of non-bonded atom-atom interactions.⁶⁵ These component interactions are a function of non-bonded distance and a set of, ideally, universal constants which are referred to as the atom-atom potentials for a given atom type pair. Therefore, by applying the argument in reverse, crystal packings may be derived with the use of such potentials.⁸⁵ The results of such calculations are usually quite reliable if only dispersive and repulsive interactions are important in crystal stabilisation. For hydrocarbons this is indeed the case and much work has therefore dealt with this category of compounds. The classical case of biphenyl has been studied⁸⁶ and it was found that the planar conformation and the stretching of the central bond characteristic of the solid state structure could be modelled accurately. Calculations on the crystal packing of *p*, *p'*-bitolyl also give values of the torsion angle within 1° of the experimental value of ca 35°.⁸⁷ Such packing calculations have also been used to describe the orientation of guest impurities in a host matrix⁸⁸ and to explain the phenomenon of chiral turnover in hexahelicene crystals through a mechanism of cellular twinning.⁸⁹

A natural extension of such techniques of minimisation of non-bonded intermolecular interactions is in the solution of the phase problem, that is in the determination of unknown crystal structures. For reasons indicated above, the crystal structures of hydrocarbons may be solved with the greatest ease. A typical example is the case of the bridged annulene in Fig 8. It was found that while the crystal symmetry permitted only six molecular orientations, five of these were prohibited on the grounds of packing energy. The final orientation gave the correct structure.⁹⁰ Another well-known example concerns the combined use of packing calculations and electron microscopy to determine the structure of a metastable phase of anthracene.⁴¹ This polymorph could not be studied by X-ray crystallography. The

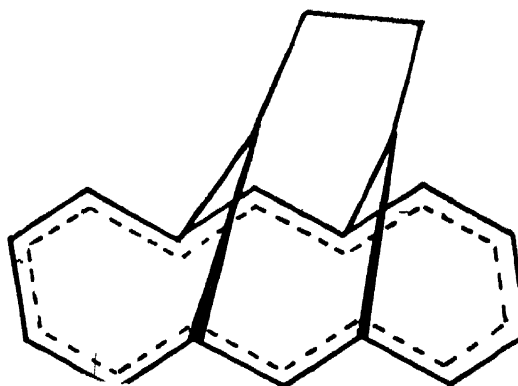


FIG 8

importance of this structure in the reconsideration of a defect-controlled mechanism for the 'non-topochemical' photodimerisation of anthracene derivatives has been alluded to earlier in this article

It has been shown that compounds containing polar functional groups are more complicated to analyse because of the more dominant Coulombic terms in the potential and poorer heteroatom non-bonding potential parameters⁹¹. Topochemical arguments have been used as an alternative to an accurate knowledge of potentials for the oxygen atom in the C-H...O bond in the crystal structure determination of the photoactive α -benzylidene- γ -butyrolactone shown in Fig. 2³⁰. This is a rare case of a fairly small molecule whose crystal structure solution proved to be unusually resistant to Direct Methods. Since the material undergoes, what was assumed to be topochemical, photodimerisation in the solid state, the starting point in the structure analysis was not the monomer lactone but an incipient dimer pair, the centroid of which was constrained to lie at the origin of the centrosymmetric space group (Fig 9). This topochemically derived starting point greatly simplified the packing analysis. The optimisation of two features (a) the plane-to-plane interactions within the incipient dimer and (b) the orientation of the incipient dimer with respect to the cell axes allowed the structure to lock into the global minimum, in other words into the correct structure.

The appearance now of faster and more powerful computers will mean that non-hydrocarbon crystal structures can probably be handled with increasing confidence. The use of even minimal auxiliary chemical or crystallographic information (unit cell parameters, topochemistry) greatly enhances the power and extends the scope of these energy minimising search programs with the result that crystal structures or, in the most general sense, structures of any molecular assembly may be reliably and accurately predicted in increasing numbers.

ORGANIC METALS

The discovery of metallic conduction in the molecular solid tetrathiafulvalene-tetracyanoquinodimethane, TTF-TCNQ (Fig 10) more than a decade ago⁹² launched one of the most highly publicised areas of collaborative research between physicists

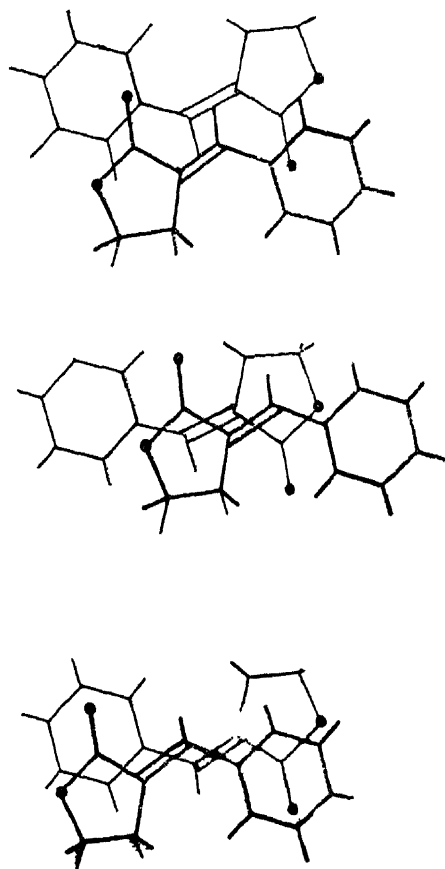
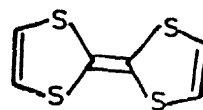
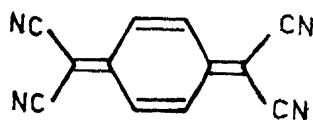


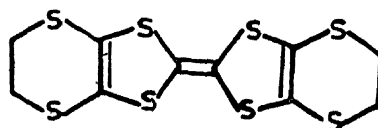
FIG 9 Some starting positions for the incipient dimer configuration in the crystal structure determination of α -benzylidene- γ -butyrolactone. The configuration in the centre led to the correct structure ultimately



TTF



TCNQ



BEDT-TTF (ET)

FIG 10

and chemists. It was realised that the molecular framework of organic compounds offered considerable scope for subtle and effective variation of structural and electronic properties. Therefore, there has been much activity geared towards the discovery of new conducting molecular solids. Such activities have involved, for the most part, novel chalcogen heterocycles and have resulted incidentally in a large body of interesting synthetic, electrochemical and crystallographic data. This field has been extensively reviewed⁹³⁻⁹⁸ and the accent here will be to show that the gaps in the area are such that they may be bridged with methods that have been developed in OSSC. Although the synthetic and theoretical efforts have been novel and varied, the structural uncertainties in persuading organic molecules to crystallise in preordained ways seems to have rendered the search for new organic metals a frustrating task.⁹⁹

TTF-TCNQ is a donor-acceptor (DA) complex and there are generally two ways of stacking D and A molecules in crystals: (a) mixed stacks in which D and

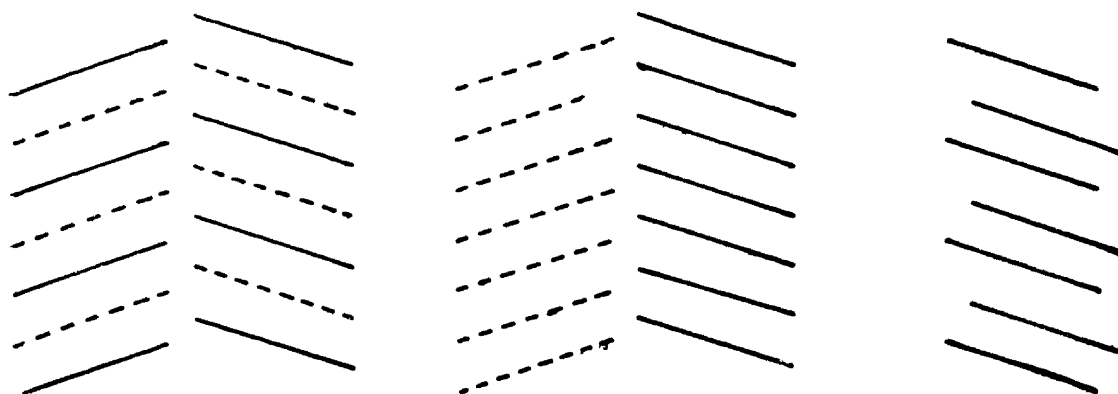


FIG 11 Mixed and segregated stacks for Donor-Acceptor complexes Peierls distortion of a segregated stack.

A molecules alternate and (b) segregated stacks in which the molecules from separated D stacks and A stacks (Fig 11). The potential ability of these two types of stacks to conduct electricity is quite different. The outstanding characteristic of the highly conducting TTF-TCNQ and related materials is the formation of segregated stacks of donor and acceptor molecules. This seemingly unlikely organisation of all the negatively charged ions into one set of stacks and the positively charged ions into another set is generally agreed to be an essential prerequisite for high conductivity in DA complexes. It is therefore extremely critical to know why compounds like TCNQ and TTF form segregated stacks while TCNQ, and other donors like, say anthracene form mixed stack complexes. Yet, the application of clearly appropriate techniques such as crystal engineering and packing calculations to predicting structural trends for DA complexes is a science still in its infancy. This gap in our present understanding of organic metals could well be because most of the work being done in this area has been conceived by solid physicists and not many structural chemists seem to be actively involved.

It has been theoretically predicted that in favourable cases, a segregated stack organic metal may exhibit superconductivity at lower temperatures and the quest for an organic 77 K superconducting substance continues fiercely. However, it is known that in a segregated stack compound there is a very high probability of a metal-to-insulator transition at low temperature (Peierls transition). The structural characteristic of such a transition is the appearance of unequal molecular separations along the stack direction (Fig 11). The Peierls transition is the most serious obstacle to be overcome in developing a molecular superconductor and in order to obtain such a substance, the transition must be suppressed. There have been three approaches to the problem¹⁰⁰. The first is the introduction of non-periodicity and many unsymmetrical donors and acceptors were synthesised to modify the Fermi surface of the low dimensional organic metal. The structural results of such synthetic manipulation are, however, very difficult to predict. The second approach is to increase the dimensionality by the physical device of high pressure¹⁰¹. In the third approach, chemical modification has been attempted to increase the dimensionality of the system. When the TTF skeleton is extended by chalcogen atoms, the

material BEDT-TTF is obtained (Fig 10). The cation radical salt of this material, (BEDT-TTF)₂I, is the first ambient pressure organic superconductor. The most striking characteristic of this salt is that the S...S non-bonded contacts perpendicular to the stack direction (parallel to the molecular planes) are actually shorter than those along the stack direction with the result that the dimensionality is greatly enhanced. An understanding of molecular packing and structure are of central importance to all aspects of OSSC and the application of these ideas to the study of one-dimensional materials has all possibilities for synergistic growth.

CONCLUSIONS

Organic solid state chemistry far from being an esoteric sub-discipline has been borrowing concepts and ideas from chemistry, crystallography and physics and in turn seems poised at a stage when it can have considerable impact on apparently quite unrelated areas of research in the physical sciences. The development of this subject might have been delayed somewhat because of unwise attempts to classify it as 'organic chemistry', 'physical chemistry', 'chemical physics', 'crystallography', 'materials research', or 'solid state chemistry'. Happily the artificiality of such attempts is acknowledged today since there are so many areas of scientific endeavour which similarly attempt to stride across the gaps between major disciplines. There is thus in organic solid state chemistry every indication for sustained and healthy progress.

ACKNOWLEDGEMENTS

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MECHANOCHEMISTRY OF INORGANIC SOLIDS

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The content of the paper is a review of the results in mechanochemistry of inorganic solids which were carried out in the Institute of Solid State Chemistry and directed by the author. The mechanochemical processes which proceed in the apparatus like mills have two main features: locality of processes and their impulse character. When processes occur in the top of the crack propagated in the solid, the transition from low energy vibron level excitation to a high one is possible. The impact of preliminary mechanical treatment on the reactivity of solids is connected with the effect of defects formed during the treatment. The results obtained are discussed in terms of technological application.

Key Words : Mechanochemistry; Locality of Processes; Mechanical Treatment

INTRODUCTION

THE reactions occurring during deformation, friction or fracture of solids have long been considered as physical phenomena and an approach to their control, optimization was based primarily on investigation of physical causes and effects. However, our experience of experimental data accumulated for the past forty years has shown that such chemical processes are significant.

Strictly speaking, the fact that mechanical action can lead to chemical consequences was not a discovery. Since the first attempts by Man to obtain fire by friction and to the more recent data on the possibility of ignition and detonation of certain solid explosives, it has come to light that chemical reactions may be initiated by mechanical means. But it was unexpected that while on one hand, the mechanochemical processes embrace a wide range of effects in nature and engineering on the other they are unusual and are not confined to reactions induced by heat evolved during mechanical action which phenomenon became known quite recently.

Striking effects have been found and unusual chemical reactions have been discovered. Thus, gold which is well known to everybody not to be attacked by oxygen of the air under ordinary conditions, at the moment of mechanical action reduces even carbon dioxide,¹ mechanical treatment of metals changes their position in electromotive series.² Oxides and salts hardly soluble even in concentrated acids being dissolving in diluted aqueous solutions of the acids and even in

water.³⁻⁷ The data are available that at the moment of mechanical action the diffusion coefficients of solids may increase many times over. At the moment of mechanical action certain compounds begin decomposing through unusual mechanism quite unlike the thermal one.⁸

At the same time the progress of present-day engineering raises a problem of development of new uncommon, non-thermal methods for initiating reactions in order to intensify such important industrial processes as the leaching of mineral raw materials in metallurgy, the activation of components of binding agents in construction industry, an increase in reactivity of ingredients of metallic or non-metallic powder-mixtures in powder technology, the new and uncommon methods for solid-state synthesis in chemical industry, etc. Taken together these factors make investigations of chemical processes, brought about by mechanical action, extremely urgent and important.

The questions which should be answered first of all are: how and where do these processes take place. The question of where these reactions proceed is not usual for classical inorganic chemistry. Indeed, when investigating a reaction in gases and liquids, except in a few special cases, the probability for the reaction to proceed is generally the same all over the bulk. Mechanochemical processes, like most other heterogeneous processes, occur locally and therefore, the question of the exact site of the reaction course is quite natural. Experience shows that it is normally either the site of contact between the reactant and an object which produces mechanical action on the system or the sites of contact between particles of the solid—where pressure and stresses are primarily concentrated.

From the sites of contact the reaction zone can spread over the neighbouring regions of the crystal due to various processes of relaxation—heating, formation of a new surface, or imperfections or chemical transformations. The rate of these processes of relaxation may be highly different. Thus, a crack in brittle solids can propagate at a velocity close to that of sound, the velocity of heat wave is determined by the magnitude of thermal gradient and by the thermal conductivity; the

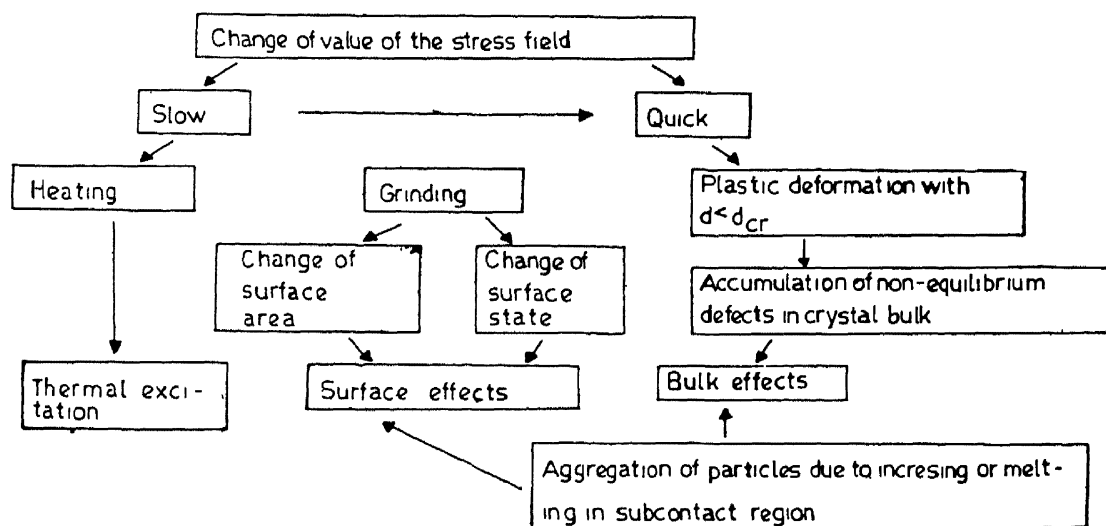


CHART 1

process of elastic stress relaxation due to formation of lattice defects may proceed very slowly requiring hours, days and even years to obtain equilibrium. The change-over from one way of stress field relaxation to another depends on the nature of substance, conditions of mechanical interaction between particles (relations between the loading of the sample and the shear), and, with other conditions being equal on the amount of energy absorbed by the solid. Chart I shows the change-over from one way of a relaxation to the others as the absorption of energy increases resulting in occurrence of the stress field. At the bottom of Chart I, chemical consequences of energy relaxation by different routes are presented.

Mechanical treatment of the system, altering conditions of the chemical reactions course, may be permanent or periodical

In the first case we have examples of change in reactivity of solids under the influence of permanent stress field generated, for example, in a Bridgeman's anvil device. It is known that these processes depend on the time of treatment, and their degree of transformation depends on mechanical work done on the system. In the case of Bridgeman's anvil device this work is determined rather uniquely by the turning angle of the anvil. These processes are well covered in detail in literature and will not be discussed in this paper.

The other case is a change in reactivity and the excitation of chemical processes in solids after mechanical treatment at regular intervals, as it takes place, for example, in various apparatus, mills. The characteristic property of such processes is their locality: the region where the process occurs is normally confined to the region of contact between the particle deformed and a grinding object, or other particles. The second peculiarity of this process is its pulsed character which we have pointed out previously.⁹ In apparatus commonly used for grinding, the formation of the stress field and its relaxation occur at regular intervals by subjecting a solid to a sequence of mechanical pulses following one after the other. A schematic representation of these pulses is shown in Fig 1. Every pulse characterises the occurrence of the stress field in the region being treated (the left-hand side of the pulse) and its relaxation leading to various physical and physico-chemical consequences (the right-hand side of the pulse)

Being characteristic properties, both locality and pulsed behaviour of mechanochemical processes, however, present experimental difficulties in studies of mechanochemical processes if the study is performed correctly (i.e. with averaging

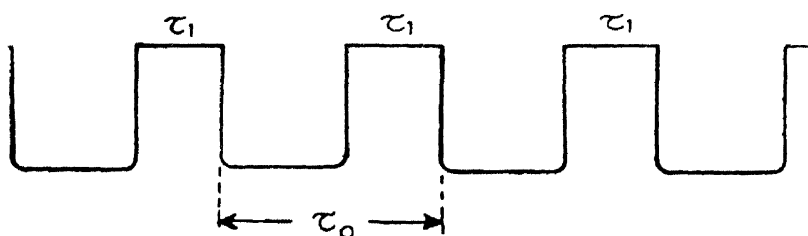


FIG 1 Pulsed character of mechanical action. The left-hand side of the pulse—the formation of stress field. The right-hand side—its relaxation by different routes

neither the site where the reaction proceeds, nor the time of the process, what some investigators used to do)

As an example of this one may consider study of chemistry of processes occurring at the tip of a moving crack. During early twenties of this century Griffith suggested that at the tip of a moving crack high temperatures and pressures were developed. Their existence was then supported by direct experimental studies carried out at Cambridge, Karlsruhe, Leningrad, and Novosibirsk. It was shown that the tip of the moving crack is surrounded by the field of high temperatures and pressures which can vary with the velocity of crack propagation and physico-chemical properties of the substance through which the crack passes.

In the early seventies in one of the papers dealing with a kinetic model of mechanochemical processes,⁹ the present author suggested that if the chemical reaction, induced at the tip of the moving crack, proceeds through several concurrent or successive stages then a change in the reaction mechanism should be expected as compared with the same reaction excited by thermal way. The concentration of energy at the tip of the crack and pulsed behaviour of the process are responsible for this.

For the last twenty years experimental data were accumulated which supported our assumption. These experiments were performed jointly by our laboratory and the physicists of the Leningrad Physico-Technical Institute^{8,10}. The set-up used in these experiments is represented schematically in Fig 2, where 1 shows the support for crystals in the ion source of a transit-timed mass-spectrometer, 2, the knife for

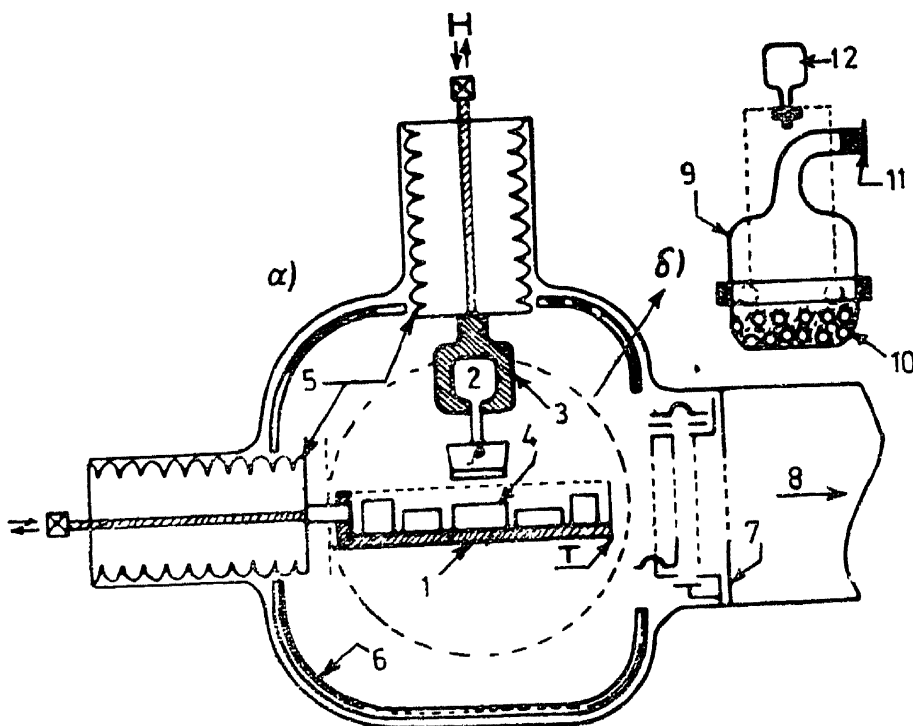


FIG 2 Schematic representation of experimental set-up for investigation of gas content formed at the tip of a moving crack (see explanation in the text)

cleavage inserted into a holder 3; 4 indicates the crystals of substance under study, 5 the system of silphons allowing the displacement of the support in a horizontal direction and that of the knife in vertical one, 6 shows the camera of the ion sources, 7 the net; and 8 the tube of the spectrometer. For example, this was shown in experiments on mechanical cleavage of alkali nitrates single crystals directly in the ion source of a mass-spectrometer. It is shown that if the velocity of crack propagation is sufficiently high, nitric oxide rather than oxygen is evolved as a gaseous product, during the cleavage of bromates from rather than oxygen is evolved, etc. The composition of products of the reaction differs from that of the thermal decomposition products. When the crack velocity decreases this effect disappeared and a usual thermal mechanism of decomposition is realized.

The cause of the observed effect appears to be the fact that at high crack velocities, the higher vibronic states are excited and at low velocities, as well as during thermal decomposition, the lower states are excited.

Recently, it has been possible to observe this effect with other compounds, for instance, iodates, chlorates, and to employ it for investigation of the crack multiplication along the curves of gas evolution.¹¹

As the first approximation, this may be shown in the following scheme in Fig. 3, where various ways of decomposition of the nitrate-ion are represented. The excitation of nitrate to the lowest vibronic state corresponds to its transition to the metastable state on account of nitrate-ion stretching; oxygen and nitrate ions are the products of the reaction. If the next vibronic state is excited (deformation of the nitrate ion by compressing rather than by stretching corresponds to it), the rupture of bonds occurs within the nitrate-ion to give nitrous oxide and the O_2^- ion.

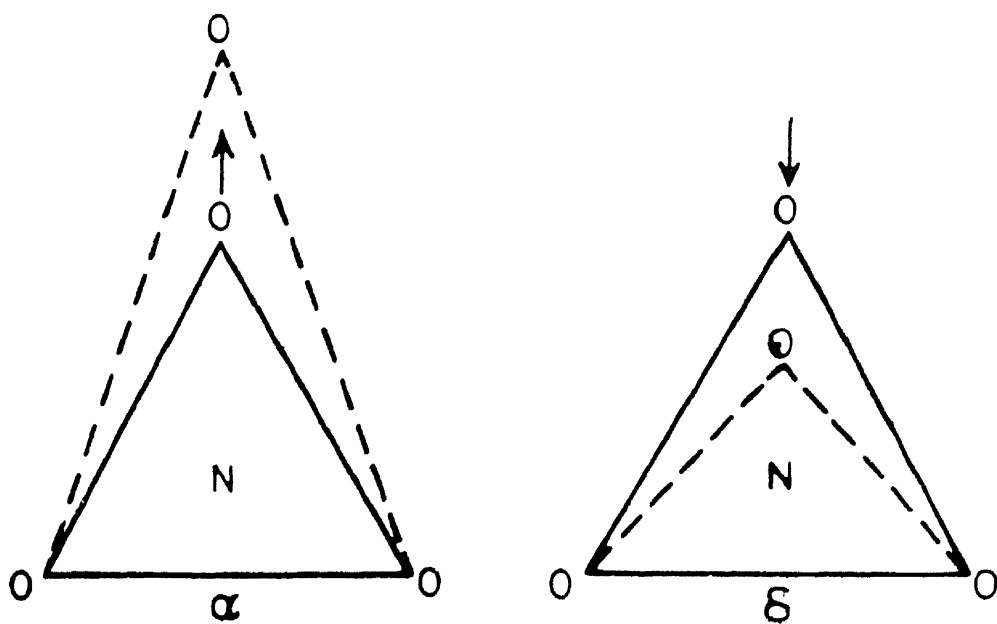


FIG 3 A scheme illustrating possible ways of the nitrate ion decomposition.

Another aspect of the question is the investigation of quick local variations in the crystal structure at the moment of mechanical action on the substance. Until recently, this problem was considered to be very difficult and even hopeless in respect of the short-lived metastable structural states¹². However, the use of accelerators as a source of synchrotron radiation, which has intensity of radiation several orders greater than that for X-ray tubes, makes it possible to study structural changes in solids during mechanical action.

The Institute of Solid State Chemistry of the Siberian Branch of the Academy of Sciences of the USSR and the Institute of Nuclear Physics devised jointly a diffractometer for synchrotron radiation which enables one to record a diffraction pattern and to put it into storage of an electronic computer in 10^{-5} sec, and also to resolve points with an accuracy of 1 hair space msec for repeated processes. Such a high resolution enables one to record the development of distortions in metals under deformation, relaxation of distorted structures, and to identify quick phase transitions. Since the intensity of the beam is high, it is possible not only to increase the time resolution, but also to follow the changes localized in small regions of the sample. Thus, during deformation of tin metal with a ruby cutter it was found that in the local regions with a size not above 0.1×0.1 mm, an increase in pressure occurs and the transformation of tin into a metastable crystalline modification with the area of stability above 10 kbar proceeds. When unloaded, the metastable modification very rapidly transforms into the stable state.¹³

Similar results concerning very strong but rapidly vanishing distortion of the lattice were obtained from silver single crystals.

In addition to detecting structural changes occurring as a result of the stress field relaxation (i.e. process relating to the right-hand side of the mechanical pulse), the synchrotron diffractometer may be used for studying processes occurring during formation of the stress field (i.e. the left-hand side of the mechanical pulse). As an example, Fig. 4 presents the results of studies on changes in the linewidth of lithium fluoride during mechanical action. It is seen that after the stress field has appeared, the formation of lattice distortions, which leads to line broadening, proceeds not immediately, but after some milliseconds.

The influence of mechanical pretreatment is another problem under study in mechanochemistry of inorganic solids. From the above it follows that, in essence, the consequences of the stress field relaxation is also the question, the consequences being long-lived. In spite of the fairly widespread opinion that the primary effect of mechanical pretreatment is the dispersion of solids and formation of a new surface, the formation of linear and point defects was found to occur along with the formation of a new surface (see Chart I). The characteristic feature is that in this case the defects are formed with non-equilibrium density and the state of solids thus obtained should be classed as a metastable one. Thus, mechanical treatment when affecting a solid by short but powerful pulses results in formation of the "active" or the so-called "metastable" state.

In connection with the great present interest shown in the properties of metastable states, their production and application in technology, we shall dwell on

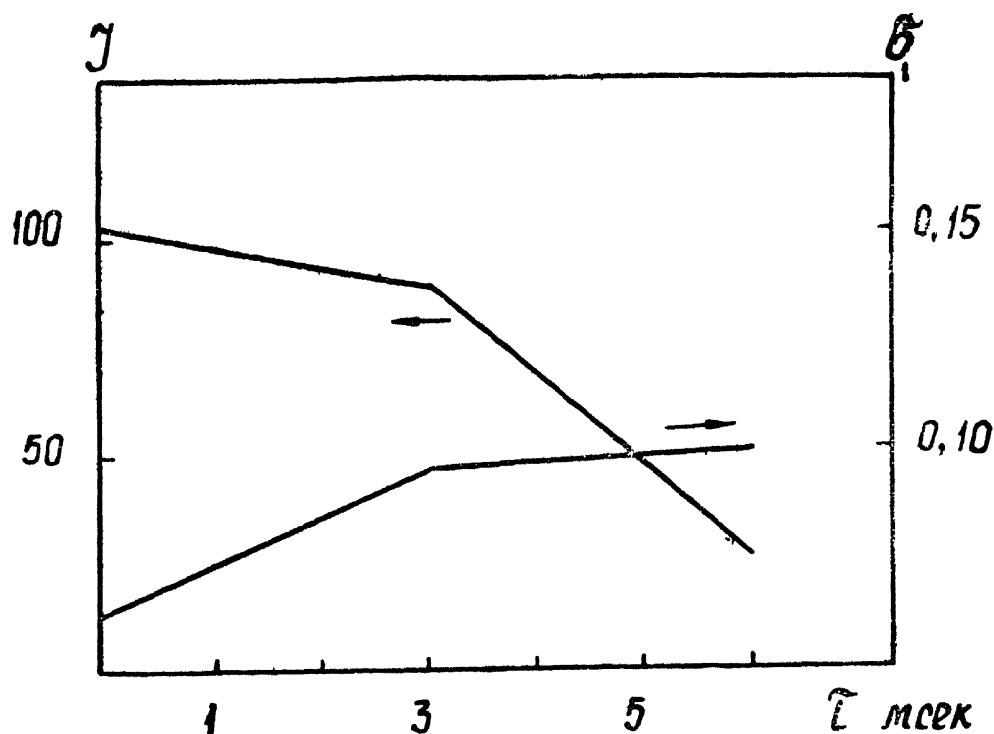


FIG 4 Change of half-width of line and amplitude in Debye diffraction pattern from lithium fluoride in the course of its deformation recorded with a diffractometer SL

this question particularly. Metastable states are known to be formed as a result of storing energy by solids and the following quenching of excited states in the crystal.

There are many various methods for obtaining metastable states. Among these are the rapid freezing of metals, and vapour condensation on a cooled surface, and intensive light and electron beams irradiation. Sometimes reactions frozen in the certain stages of their course are used for this purpose. Plastic deformation of a solid may be also used to obtain metastable states. As it is seen from Table I, the mechanical method for obtaining metastable states may lead to three basic types of sources of metastability: compositional, structural and morphological. A fairly large amount of energy accumulated by a solid is achieved (0.2–0.8 RT).

There are two approaches to estimate the influence of mechanical pretreatment on the reactivity of solids. One of them takes into account an increase in the free energy of solids occurring as a result of increase both in enthalpy and entropy terms in the equation for the Gibbs thermodynamic potential in the course of mechanical treatment. A change in the potential (or the free energy, since the solid state is the question) may be defined using the notion of activity A introduced by Huttig¹⁴

$$G^* - G = A^*$$

As the free energy changes so the equilibrium constant related to it by the relation $\Delta G = -RT \ln K_0$ must also change. An increase in activity as a

TABLE I
Methods of obtaining metastable states

Methods	Types of disturbances	Rate of quenching sec ⁻¹	$E, RT_m/10$
<i>Quick Cooling of Melt or Crystal</i>			
(a) freezing of melt on cooled surface	<i>S</i>	10^3 – 10^5	0.2–0.4
(b) Lazer melting		10^{18}	0.8
<i>Condensation</i>			
(a) of vapours	<i>C</i>	10^{12}	0.9
(b) electrochemical			
(c) chemical	<i>M</i>		
<i>Irradiation</i>			
(a) with heavy particles	<i>C</i>	10^{12}	0.5
(b) ionic implantation			
(c) cross beams condensation			
<i>Action of Mechanical Pulse</i>			
Mechanical apparatus	(a) free shock	10^{+1}	0.2–0.8
	(b) shear		
	(c) shock + shear		
Shock waves		10^{18}	
<i>C</i> —compositional			
<i>S</i> —structural			
<i>M</i> —morphological			

consequence of mechanical treatment both for exothermal and endothermal reactions always lead to increased deviation from equilibrium and therefore to increased reaction rate

The storage of the excess energy accumulated by a solid can be checked either by calorimetric measurements (for example, by determining heats of dissolution) or by using DTA technique^{17–19} (as a difference between enthalpies of activated and non-activated samples)

The other approach to estimation of effect or preliminary mechanical treatment is in consideration of properties of specific defects generated during mechanical treatment, and of peculiarities of solid-state reaction mechanism.²⁰ Not only is the amount of energy accumulated by a solid important for accelerating one or another chemical solid-state reaction, but the types of defects involving this energy are also of importance. The point is that depending on what mechanism of the reaction is and what step is rate determining, different chemical processes are sensitive to various types of defects in a different manner. Therefore, the task of investigation is to find, which defect this reaction is especially sensitive to, in order to select such a way of treatment of a solid, which involves the maximum concentration of these defects.²¹

With such a statement of the question one can not restrict oneself to measuring integral quantities such as excess heat of dissolution, X-ray line broadening, etc. The problem inevitably arises to obtain by various physical methods a direct information on what processes occur during mechanical treatment and what defects are therewith generated. As an example of such an approach, the results of investigations undertaken by us jointly with the Institute of Physical Chemistry of the Academy of Sciences of GDR can be cited. These investigations were carried out on mechanical activation of apatite with the aim of developing new methods for obtaining phosphate fertilizers without processing the ore by acid^{22,23}. As is well known, this problem confines to the increase of reactivity of apatite towards acids. Apatite is hardly soluble in aqueous solutions of weak acids therefore, it should be expected that the rate-determining stage of the process is not the processes of transfer through the layer of saturated solution which borders on the surface, but a chemical reaction on the surface.

The mechanism of this reaction is in the reaction of complexing between ions of the ligand available in the solution or water molecules (if it is aquacomplex) and cations or anions composing the lattice. Whether the ions go into the solution or the process confines to the adsorption of the ligands on the surface depends upon the relation between the energy required for removing the ion from the lattice and the energy released as a result of interaction between the ligand and the ion of the complexing agent. With a given composition of the solution we can alter the first of these two components by generating various crystal defects which loosen chemical bonds in the lattice. Dislocations and boundaries of blocks may be such defects first of all. Therefore, the treatment of a solid with high-power mechanical pulses leading, as was said, to the formation of such defects may be used as a method for increasing the reactivity of apatites and phosphorites. Recently, Australian chemists have managed to show by direct observations with electron microscope that it is dislocations which are the sites where the dissolution of apatite crystal begins.

Experimental investigations undertaken by us have shown that, in fact, if mechanical treatment results in plastic deformation and accumulation of defects in

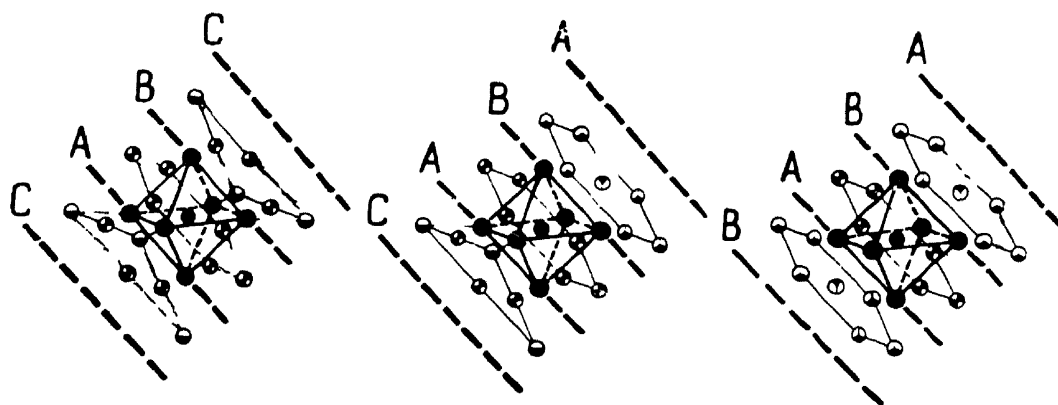


FIG 5 A scheme showing the change in environment of the iron-oxygen group in the course of mechanical treatment (A) crystallochemical scheme, (B) relative position of cations

apatite crystals (as determined from line broadening in Debye diffraction patterns and changes in structure of EPR spectra for paramagnetic marks in apatite crystals), the solubility of apatite in initiators of soil acids—the solutions of ammonium citrate and citric acid increases. In some cases this increase may be fifteen-fold or even twenty-fold, allowing the mechanical treatment of apatite to be used as a non-acid method for preparing phosphate fertilizers.

If mechanically activated apatite is heated to 350–400 °C the crystal defects are annealed and hence the reactivity of apatite decreases.

In contrast to the activation of apatite, where the accumulation of energy occurs due to the formation of the large number of dislocations, the mechanical activation of ferrites offers an instance where the formation of metastable states takes place due to the redistribution of three- and two-valence cations over octa and tetra-positions.^{26–28} Experimental data, obtained in our Institute, have shown that, in the course of mechanical treatment, it is to carry out the deformation of the crystal in such a manner that the shear of the oxygen planes with respect to each other is realized. The displacement is especially considerable in the (111) planes where they are shifted on vector which is shorter and not coincident with the vectors of the face-centered cubic oxygen lattice typical for spinels. As a result, the spatial arrangement of oxygen ions exhibits no long-range order through the cubic close packing of oxygen sublattice is retained. Locally, the oxygen sublattice may comprise, for example, a superposition of cubic and hexagonal layers. In consequence, the number of the nearest octa-sites corresponding to the angle of the cation-anion-cation bond changes (Fig 5). This bond is known to be responsible for the main physical and chemical properties of spinels. As this takes place, there appear exchange-bound pairs cation anion-cation with an angle of the bond different from the right angle (90°) typical for common ferrites-spinels (Table II).

TABLE II

The number of the nearest octa-sites for an arbitrarily chosen cation as a function of the type of oxygen sublattice packing in spinels

Local type of oxygen sublattice packing	The number of the nearest octa-sites corresponding to the angle of the cation-anion-cation bond			
	71°	90°	122°	180°
Cubic CA (cation) BC	0	12	0	6
Hexagonal BA (cation) BA	2	6	12	0
Hybrid I BA (cation) BC	1	9	6	3
Hybrid II CA (cation) BA	1	9	6	3

Due to this, a change in magnetic properties of spinels takes place. Mechanical activation results also in amorphization of structure. The model of the structure of amorphous solids is a random close packing of rigid spheres.²⁹ According to

this model, the vacant large octa-sites have the highest occupancy probability in the oxygen sublattice³⁰ This is also supported by experimental data of the Mossbauer spectroscopy, according to which, all the cations initially occupying tetrahedral interstices are moved into octa-positions in the course of mechanical activation²⁷ The physical consequence of this influence upon ferrites spinels is an increase of magnetic ordering during mechanical activation (fact is of interest by itself, since we used to think the reverse). The chemical result is unusual properties of spinels treated in such a way. Thus, it is well known that when treating zinc ferrite with acid solutions, the zinc cations are leached out from zinc ferrite in the first instance, then the three-valency iron ions go into the solution In the case of mechanically activated ferrite, the opposite picture is observed³¹

Thus, mechanical activation leads to a new method of obtaining amorphous ferrites-spinel Its obvious advantage is the possibility to carry out amorphization through several stages and to control the degree of disordering at each stage.

Similar results are obtained for other compounds related to ferrites-spinels in structural type For example, in the case of binary sulphides, mechanical treatment leads to the change of iron coordination from tetrahedral to octahedral.³²

The use of mechanochemical methods for intensification of processes occurring between solids offers radically new and promising possibilities. It is well known that the rate of these reactions in their initial stages is determined by the number of contacts between the reactant particles and by the area of these contacts. As the reaction proceeds, the resulting layer of the solid product separates the reactants, and the diffusion of the reactants through the product layer becomes a rate-determining stage of the process. Conducting simultaneously mechanical treatment and heating one may achieve a permanent renewal of contacts between solid particles and permanent change of the reaction mechanism from the diffusion range to the kinetic one.⁶ Thus, it has been shown in a paper³³ that if a mixture of oxides forming ferrite is heated and treated simultaneously in a vibratory mill the temperature of the synthesis can be decreased by several hundred degrees

If, along with two components, there is a liquid in the system, for example, water and the relation between the solid and liquid phases is so that the solid particles can form a labile framework structure,³⁴ it may be expected that when a mechanical pulse is delivered to the system a pressure pulse initially occurs in the system Since the liquid is more mobile than the solid particle forming the frame the liquid will pass from the region of elevated pressure to the region with lesser pressure The filtration of the liquid through pores will lead ultimately to elevated temperature, so some time there will be condition of elevated pressures and temperatures in the system In Fig 6, the shaded area corresponds to these conditions This enables one to realize mechanochemical processes, such as hydrothermal synthesis pressure leaching, which require special apparatus⁹

Finally, the so-called "mechanical alloying" should be also classed to the processes occurring between solids This process is in obtaining metastable states

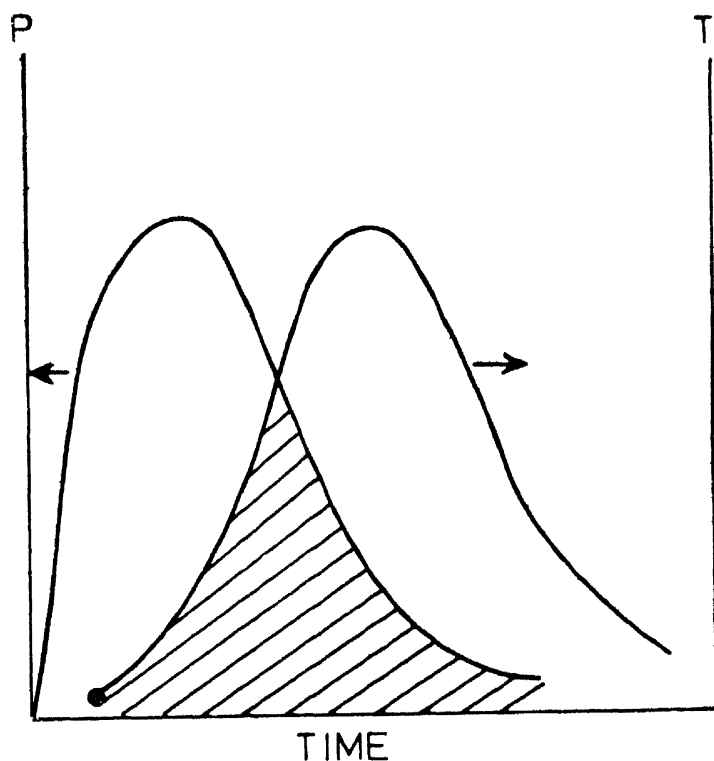


Fig 6 A scheme showing the occurrence of high pressures and temperatures during mechanical treatment of pulp

due to the consequent alternation of the grinding and welding stages is mixtures of two metal powders^{35,36}

Not concerning with the physical and metallographic consequences of mechanical alloying, well known from literature, we shall dwell here in more detail on the chemical consequences of mechanical alloying. Very often mechanical alloying leads to a sharp increase of reactivity of solids. The formation of the so-called supercorroding alloys for the quick preparation of hydrogen from water can be cited as a good example³⁷

Another example is a rise in reactivity of metals towards hydrogen during their treatment in mixture. Thus, mechanical alloying of a mixture of magnesium and nickel powders results in an increase of reactivity up to the level close to that which is reached in this mixture by the way of fairly complicated technology comprising several alternating stages of melting and sintering of resulting powder^{38,39}. An increase in reactivity of the metallic mixture takes place not as a simple result of increased interphase surface but as a consequence of formation of defect region bordered on this surface. Thus, experimental data obtained in our laboratory have shown that in mechanical alloying of a mixture of magnesium and nickel the displacement occurs, favouring the process of hydrogenation.

III. TECHNOLOGICAL PROBLEMS—THE USE OF MECHANOCHEMISTRY, THE CHOICE OF AN ACTIVATOR AND REGIME OF MECHANICAL TREATMENT

Based on the above scientific approach to the understanding of mechanochemical processes and changes of reactivity of solids in consequence of mechanical treatment,

it is also possible, in a number of cases, to make specific recommendations or intensification of technological processes with the methods of mechanochemistry and on the choice of apparatus for this purpose.

The first that one should know in such an approach is the peculiarities of the process which is to be controlled and first of all which stage of the process is rate-determining. Knowing the rate-determining stage and the peculiarities of the process we should determine then to which type of defects the process under study is especially sensitive and which conditions must be realized for its best course. Depending upon the peculiarities of the process all the processes can be divided in several groups so as it is shown in Table III. In the left column of the table the

TABLE III

Type of transformation	What is to be changed upon mechanical treatment	Examples
$^I T \rightarrow T(S)$	<i>S</i> Surface, number of active sites	Preparation of (a) minerals of flotation (b) preparation of fillers for composites (c) Preparation of sorbents
$^{II} T \rightarrow T(V)$	<i>A</i> Generation of non-equilibrium defects in crystal bulk, point, one-dimensional, two-dimensional, face of blocks	(a) Polymorphous transitions (b) Tetragonal displacement (c) Abnormal distribution of ions in lattice (d) Topotaxical transformation
$^{III} T + L(G)$	<i>S, A</i> Surface, presence of defects in crystal structure	(a) Reduction of oxides with hydrogen (b) Leaching of ores (c) Formation of carbonils (d) Grouting
$^{IV} T + T$	<i>S, A, N</i> Surface, Presence of defects, number of contacts between particles	(a) Preparation of titanates, ferrites, aluminosilicates by reaction solid-solid (b) sintering of solid-phase mixtures
$^V T + T(L) \rightarrow TM$	<i>S, A, N</i> Surface Presence of defects number of contacts, local increase of N at points of contacts	(a) Preparation of metastable solid solutions of alloys (b) Hydrothermal synthesis

type of the process is given, in the middle—the factor (or factors) producing decisive influence on the course of the process. In the right column, the examples of specific processes are given.

Assume that the process takes place on the surface and its rate is determined by the value of specific surface or by active sites on the crystal surface as it takes place, for example, in flotation when the sorption of flotoreagents by minerals occurs, in the preparation of high-filled polymers, catalysis, etc. In these cases, the chief condition for conducting mechanical treatment must be the realization of such regime which provide the maximum disperisation of the solid at minimum power expenditures

In the case when the process comprises a transformation involving the rearrangement of the crystal lattice and this transformation may be facilitated, in contrast, or hindered under the influence of various defects mechanical treatment must be carried out in the activation regime, i.e. plastic deformation must be the main channel of the elastic stress field relaxation. This is the case, for example, if one needs with the help of mechanical treatment to carry out the transformation of one polymorphous modification onto another, to obtain the abnormal distribution of ions on interstitial sites, to conduct the mechanochemical decomposition of a solid. If the transformation, which is to be affected, has a cooperative character e.g. martensitic transitions by incorporating defects into the lattice with the help of mechanical treatment one can prevent the polymorphous transition rather than accelerate it. This is the case, for example, in the transformation of tetragonal modification of copper ferrite into the cubic one ⁴⁰

The peculiarity of the processes which course or intensification require activation is the availability of the threshold energy of mechanical pulse, below which activation does not take place. This markedly restricts and, sometimes, make impossible the employment of apparatus with low power intensity (for example, common ball mills) for activation.

Such processes as the leaching of minerals and rocks, the reduction of oxides with gaseous reducing agents, various reactions of inorganic synthesis involving interaction of a liquid or gaseous reactant with solids which beings on the surface and then propagate into the bulk crystal, all of them for require course the maximum contact of reactants, on the one hand, and the availability of potential centres of the reaction — defects in the solid phase, on the other. Since the first is realized by the way of fragmentation of the solid component of the reaction and the second—due to its activation, one should chose such a regime of mechanical treatment which involves both the grinding and activation of the solid.

When conducting such solid phase processes as the synthesis of ferrites, silicates from solid components one should add to the two above factors—the value of specific surface and crystal activity and the third—the number of contacts between particles of the solid components. Thus, it is essential to conduct mechanical treatment of each component and then that of mixture so as to grind, activate and mix both the components. Thus, in preparing the solid-phase mixture to the reaction and in the course of the reaction one should be able to control not

only the processes of grinding and activation, but also the mixing process of the components

Finally, the course of some solid-phase processes requires besides the above three factors another one. the generation of extreme values of temperature and pressure at the point of contacts between particles of the solid at the moment of mechanical action. This leads to the possibility of obtaining metastable compounds and states at the sites of contact and their following quenching. Mechanical alloying and hydrothermal synthesis, which we have mentioned above, may be examples of such processes. For their course, besides factors providing the contact of the reactants, i.e. surface, particles, the number of contacts between particles of different components and activity of solids, associated with defects available in them, a sufficiently high-power mechanical pulse is required to create extreme conditions at the point of contact.

From the above-stated it is seen that different processes require different regimes of mechanical treatment. This determines also the choice of apparatus for conducting mechanical activation. In spite of the apparent variety and diversity of apparatus applied in mechanical activation, all of them can be divided into three main classes depending on the character of elementary physical processes providing mechanical action (Fig. 7). The process of mechanical action, which confines mainly the operation of shear is realized in various apparatus such as rollers of cone-type, crushers, etc. The collision of a moving object with a barrier is realized in various apparatus such as jet-mills, disintegrator, etc. Peculiarity of these apparatus is that the action is produced upon each specific particle.

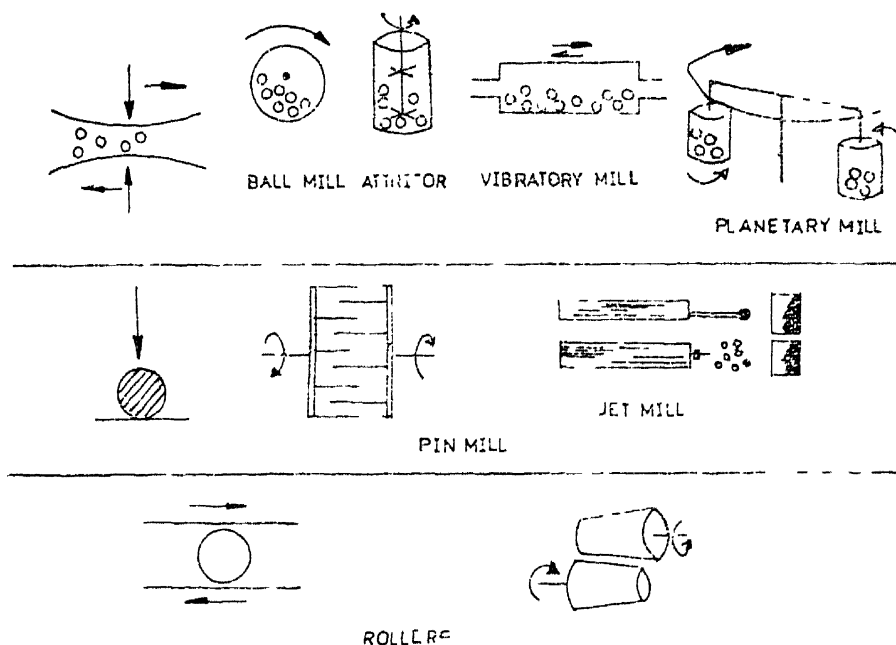


FIG 7 Types of mechanical action when employing various machines for conducting mechanical activation

And, finally, numerous grinding apparatus, from ball mills and to vibratory, planetary, mills, and attritors a combination of shock and shear loading is realized. In contrast to apparatus of jet-mills type, these machines enable one to carry out the solid state reaction between particles of specific components and, among these the presence of liquid phase. Taking all this into account, one can recommend common apparatus for grinding applied in industry, i.e. mills for realization of the processes of the first group showing in Table III. The chief criterion for their application is both productivity and economical operation. For the solution of some specific problems some specific requirements are necessary (for example, such as the prevention of contamination of the sample, etc.). In the case of the processes relating of the second group, the value of energy pulse delivered to a solid is of importance and the expected effect is achieved only with the existence of some threshold energy or special character or pressure—shear relation during deformation. The employment of common grinding apparatus—mills for activation dose not give the desired effect and it is necessary to create special apparatus with high power intensity and sufficient time of system being under extreme conditions (such as planetary mills, attritors, vibratory mills with large amplitude, etc.).

The employment with this aim of jet-mills, desintegrators is restricted in spite of their high power intensity, because of the little time of excitation of the system. For intensification of the processes relating to the third group, where simultaneous increase of the surface and its activation are required, it is essential to carry out the operation of mechanical treatment at first in the regime of grinding and then in the regime of activation. This can be done either by the consequent use of two apparatus: mill and mechanochemical activator or due to the work of one activator in different regimes. Recently, new types of apparatus have appeared in which these two consequent operations are carried out simultaneously.⁴¹

Finally, the processes relating to the fourth and fifth groups in Table II can be carried out in apparatus where mechanical action is produced not upon a specific particle, but upon some number of them. If in doing this besides a simple increase of the surface and the number of contacts between particles, the reactivity of the components is also important, a requirement arises that mechanical pulse should be of sufficient power. This confines the field of application of apparatus to vibratory mills, attritors and planetary mills.

In conclusion, a few words should be said on the procedure of choosing a method of mechanochemical treatment for solving specific technological problems. It must comprise in our opinion, several research stages.

1. Based on the peculiarities of the reaction mechanism one should determine which type of defects the reaction is especially sensitive to.

2. To determine which form of mechanical action should be chosen in order to obtain maximum concentration defects with minimum power input. What a correlation between shear and pressure must be, what an amplitude pulse and its duration must be, whether there is a correlation between the time of system being in metastable high excited state and the time needed for the completion of the reaction. In doing this it is important to take into account a necessity of precise

measuring delivered in the form of mechanical pulses. Deviations from this rule both with insufficient power of mechanical pulses⁴²⁻⁴⁴ and with excess energy delivered to the system⁴⁵ or excess time of treatment⁴⁶ lead to considerable decrease in efficiency of mechanical activation and sometimes even to the reverse effect.

3 Then one should determine how the shear stress and pressure are distributed among the particles and how to obtain optimum conditions. Specific realization depends upon the type of apparatus used for mechanical activation. If in the case of jet-mills or disintegrators the problem confines mainly to the consideration of collision between a particle and a barrier, in the case of ball mills and similar apparatus with high power intensity (attritors, vibratory and planetary mills), the distribution of pulse loading among the particles is the main thing.

4 Finally, one should imagine how to repeat optimum conditions of the treatment of a power or a particle in order to calculate the required productivity of apparatus.

Additional requirement to be taken into consideration depending upon specific conditions of the process are such as minimization of the wear of working parts of apparatus, possible causes of contamination of the probe, reduction of specific quantity of metal and power consumption of apparatus.

It is quite clear that all this procedure of choosing a method may be realized when necessary investigations in the field of mechanochemistry of inorganic substances—the subject of the present lecture—will be carried out.

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